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THE THEORY AND PRACTICE
OF
ENAMELLING ON IRON AND STEEL
WITH HISTORICAL NOTES ON THE USE OF ENAMEL.

BY

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LONDON:
CHARLES GRIFFIN & COMPANY, LIMITED
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1917.

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PREFACE.

THE manufacture of enamelled ware is carried on to greater extent in Germany and France than elsewhere. This treatise is from the pen of a German technologist of wide experience in enamel works, and who is now the chief chemist and director of large works in the French centre of the industry. The book deals more especially with the process of enamelling hollow-ware. It gives a description of the raw material used in enamelling; it explains the action and the effect of each substance, and states the chemical combinations which take place. A number of mixtures are given for obtaining given effects or colourings. The process of enamelling is followed up in detail from the mixing, melting, and grinding of the enamel components; the annealing and pickling of the sheets and castings; the application of the enamel; the burning, decorating, etc. It also compares utensils made of enamelled ware with similar ones made of nickel and aluminium.

The book abounds in instructive matter which throws much light on the intricacies of a branch of industry in which very few people are posted, and it is hoped that this English edition will be found of great service.

October 1909.

Reprinted March 1917.

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ENAMELLING ON IRON AND STEEL.

CHAPTER I.

INTRODUCTION.

ENAMELLING, which was for too long regarded as an insignificant though interesting industry, has, commensurate with its extraordinary growth during the last ten to fifteen years, become of considerably increased interest and importance. An industry of which the total output in Germany alone is estimated at about £3,000,000 annually, and which directly employs 20,000 workers in that country and from 12,000 to 14,000 in Austria-Hungary, has established its title to economic existence.

Its growth dates from the time when the empirical worker in the factory was displaced by the scientifically trained technologist, who, investigating methods hitherto jealously guarded, developed them ; and our industry has this in common with most others of importance, that while earlier generations of workers sought from an empirical standpoint to remove such defects as made themselves manifest, it is their successors, the trained men, who have succeeded in divining the cause of the faults and so removing them, and who, in addition, are able by a study of the chemical and physical properties of enamels to select the most suitable raw materials and use them to the best advantage.

In this manner the industry has not only been able to keep pace with the constantly advancing price of raw materials, such as felspar, tin, tin oxide, cobalt oxide, coal, sheet metal, and also wages, but by simplification of production and improved methods has won its way into popular favour and increased general use.

For the progress attained, however, it is not only the up-to-date worker that has to be thanked, but the fortunate circumstance that manufacturers have everywhere been found ready to encourage every advance, even by costly and often fruitless outlay. These men, with their untiring activity, have been a source of inspiration to their juniors; and the latter, with sound theoretical knowledge and high ideals and aspirations, applied themselves to this new calling which had lain so long outside the beaten track of technical activity.

Trying work, many cares, and frequent reverses awaited their efforts; but so much the greater was the sense of satisfaction when a new advance was chronicled, renewing the vitality of the industry, and indicating fresh channels for its development.

Owing to the exceptional nature of the enamel industry, its literary treatment has been but meagre in character, the existing literature being hitherto of very inferior quality, since it is either entirely obsolete, or at the most only up to the standard of the uninitiated. It is true that a few actual treatises for the worker are in existence,* but in general one thinks of literature dealing with enamels as consisting more or less of disguised enamel formulæ. This degraded materialism on the part of the majority of experts may keep many a searcher after manufacturing recipes from the existing publications. It must be stated, moreover, that the publication of formulæ not only frequently entails a breach of confidence, but may also be absurd and misleading.

It is hardly necessary to state that one and the same formula is not suitable for all work, and that the chemical composition of the materials employed, of the sheet metal, the kind of fuel, the muffle and smelting furnaces, and the methods adopted in the enamel works themselves, have a definite influence on the composition of an enamel formula. The true expert will easily be able, after a short time, to prepare on demand the most suitable enamel possible for a given work. The difference between the formulæ often lies in quite small but nevertheless important deviations, since in essentials the nature of the formulæ is the same everywhere; for the

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I gladly make an exception in the case of the interesting economical study of Dr H. Wuppermann, on *The Industry of Enamelled Hardware in Germany*.

enamels are chemical compounds, which are only capable of variation between certain narrow limits. Again, value and knowledge are not to be gained from the formula-book, but from experience and intelligence.

Finally, the technologist's experience of the process is not his exclusive property, for though he may in the main thank his own intelligence, yet almost always his knowledge has been acquired at the owner's expense.

CHAPTER II.

THE RAW MATERIALS.

Felspar.—This important material is obtained almost exclusively at the present time from Norway. The felspar may often safely be replaced by an indigenous mineral such as one finds in Bohemia, where it occurs in sufficient quantity and purity. A good felspar should be colourless, or at the most appear faintly yellow (*Mosserfelspar*) or maroon, and should possess the following composition as nearly as possible :—

Siliceous earth . . .	65·0	per cent.
Alumina . . .	18·0	„
Alkalies	16·5	„

The purer the felspar and the less it is contaminated by iron oxide, etc., the whiter will be the enamel.

The table on page 6 shows the composition of the felspars according to the locality where found.

As regards its use, the felspar should be obtained in lump only, as opposed to the increasing employment of powdered spar, for in this way only has one the certainty of always buying the same product, free from admixture with cheap quartz, etc. An analysis made at the time of purchase is well worth doing, but the expert knows the nature and value of the felspar by merely looking at a specimen.

Two felspars, moreover, possessing the same chemical composition, may have a different influence upon the enamels prepared from them, according to the mines from which they are obtained. The cause of this phenomenon may depend on molecular conditions, but as yet has not been investigated.

	Felspar from					
	Norway.	Bohemia.	Halle.	Fichtelgebirge.	Bavaria.	France, Chanteloup.
Siliceous earth . . .	64·44	63·11	62·76	70·10	61·37	64·00
Alumina . . .	18·75	19·70	19·20	17·16	20·23	20·56
Lime and magnesia . .	0·27	2·27	0·64	1·43	0·55	0·38
Potassium oxide . .	13·82	14·57	14·90	1·52	15·75	14·99
Sodium oxide . . .	2·40	...		8·65	...	..
Iron oxide . . .	0·65	0·45	...	0·01	0·45	
Water + waste . . .	..		1·70	...	1·31	...

The expensive and now obsolete process of making the felspar red-hot and then disintegrating it before grinding is superfluous. Great care must, however, be taken that the felspar is not contaminated by earthy matters, coal, etc., such as may be gathered from the ship and truck. In such cases the fragments of felspar may be sieved and washed.

The smaller pieces are ground apart for use in the preparation of ground or of blue enamels.

Quartz. — An important and usually unadulterated product which may safely be purchased in a powdered condition.

In many places the quartz has been replaced with advantage by beautiful white river-sand, bodies which chemically are silica, or, in other words, pure quartz. The best substitution, however, is made where enamels are prepared from river-sand, not from quartz.

Concerning the origin of the use of felspars, quartz, and especially clay little is known.

Fluorspar.—Only the best and purest qualities of fluorspar or calcium fluoride may be employed, especially for white enamels. The difference in price between the various qualities is not material, in view of the relatively small amounts of fluorspar consumed. Great care must be exercised in taking the correct quantities, since excess of lime is always detrimental; while for ground-enamels fluorspar is avoided as far as possible.

Borax.—This compound has the advantage of being less complex, more agreeable, and more certain in its action than a mixture of boric acid and soda. Borax crystallising in the monoclinic system with ten molecules water of crystallisation ($Na_2B_4O_7 + 10H_2O$) must be distinguished from that crystallising in the regular system and containing only five molecules of water.

We are only concerned with the former substance, which melts at a red heat with a loss of 47 per cent. of its water of crystallisation, and dissolves easily in hot water (200 parts of borax in 100 parts water). Specific gravity = 1·69.

Borax must not be stored in a position exposed to the air, as it attracts moisture, alters in weight, and so causes an error in admixture. For the same reason the moisture content of a borax consignment is determined at the time of its arrival, in order eventually to obtain compensation from the consignor. Up to as much as 6 per cent. of moisture may be fixed during transit, and the effect of this in a large enamel works needs no further discussion.

Borax is imported in the form of very fine powder. In those works which manufacture their own borax, it is carefully dried by being left a sufficient time in the centrifugal machine, and then ground as fine as grain. The finer the powdered borax is, the more intimate will be the mixture with the remaining enamel constituents, and in consequence the more uniform and beautiful the enamel. Generally speaking, the preparation of one's own borax is inadvisable, since various disturbing factors may arise; but, in addition, the manufaoture of too many separate products for home consumption is not economical. Here the law governing division of labour consequent on specialisation holds good, and those chemical firms which are engaged more or less exclusively in the manufacture of borax, the production of metallic oxides, colours, etc., will always be more capable of taking up work or of entering into competition.

Boric Acid.—In places where boric acid is used, the chemically prepared pure substance, which never changes in character, is preferred to the discoloured Tuscan variety.

Soda and Potash.—These bodies give the enamel a bright lustre, but excess must be carefully guarded against. Soda is to be preferred to the more expensive potash (potassium carbonate), since the action is identical. The term soda is used for the body corresponding to the chemical formula $Na_2CO_3 + 10H_2O$, but in practice only calcined soda is employed, being anhydrous sodium carbonate in powdered form.

This calcined soda, containing 41 per cent. carbonic acid and 59 per cent. sodium oxide, is stored in a dry place, since it is highly deliquescent and liable to form lumps. As in the case of borax, so with soda: only a very finely powdered condition is employed.

Saltpetre.—Sodium-saltpetre ($NaNO_3$) is cheaper than the potassium salt (KNO_3) and acts in identically the same manner. It is added in quite small quantities to the enamel mixture, and its primary function is to decolourise. To blue enamel very little saltpetre is added, or, even better, none at all. After common salt, the most hygroscopic body is saltpetre, and this is stored in boxes lined with tin-plate and capable of being made air-tight.

Cryolite.—Both natural and artificial cryolite are procured and employed for this industry. Recently many sodium silico-fluorides have been used, these being obtained for the most part as by-products in the manufacture of artificial manures, etc. In the above, the removable hydro-fluor-silicic acid is taken up by water, and the sodium silico-fluoride precipitated from this solution by the addition of soda. Many works use common salt for the same purpose. Before using such a sodium silico-fluoride, a warning must be given that sodium chloride is always present, and a sodium silico-fluoride prepared through the agency of common salt is recognised by its poor colour and disagreeable odour. A simple analysis such as the following quickly shows the presence of chlorine. A sample of the body in question is boiled with distilled water, filtered, the filtrate acidified with a little chemically pure nitric acid, and a few drops of lunar caustic or silver nitrate solution added, whereby a chloride will separate out as a white, curdy precipitate. A faint white turbidity indicates nothing. A convenient quantitative method for estimating sodium silico-fluoride is as follows :—A weighed amount is taken, dissolved in hot water, and the solution titrated with 2N (twice normal) caustic soda, using phenolphthalein as indicator. The calculation of the amount of pure sodium silico-fluoride present is given by the following equation :—

$$Na_2SiF_6 + 4NaOH = 6NaF + SiO_2 + 2H_2O.$$

Commercial sodium silico-fluoride contains 90–95 per cent., and has been employed with much success, partly displacing the natural cryolite, although for more expensive wares, and in the case of blue enamel, the natural cryolite is preferable.

The so-called artificial cryolite which is used possesses a variable composition, depending on the vendor and on the price. The more inexpensive it is, the more quartz or silica it will contain, so that here good quality and cheapness do not go together.

One sample of an artificial cryolite had the following composition :—

(1) 95 per cent. sodium-aluminium fluoride ($6NaF + Al_2F_6$).
5 " silica.

For manufacturing purposes this quality is most suitable, and almost entirely corresponds to natural cryolite. The ratio of $Al_2F_6 : NaF = 40 : 60$, *i.e.* normal.

Another sample was made up as follows :—

(2) 80 per cent. sodium-aluminium fluoride.
20 " valueless quartz.

Naturally this was less expensive.

Finally, a still further interesting composition was exhibited by another variety :—

(3) 18 per cent. Al_2F_6 (aluminium fluoride).
50 " NaF (sodium fluoride).
32 " SiO_2 (silica or quartz).

A fourth contains :—

(4) 26 per cent. Al_2F_6.
40 " NaF.
32 " SiO_2.

From the above examples we learn possible variations and causes of failure in enamel preparation. It would not be correct, however, to deny every advantage to artificial cryolite, for when the composition is similar to No. 1 above, then the natural cryolite may be safely replaced, if the difference in price allows. When making a purchase there must be a guarantee as to the composition of the product, and frequently an analysis is desirable.

It is obvious what an injurious effect a cryolite substitute containing 32 per cent. quartz must have in the preparation of enamels by an unsuspecting manufacturer who, unwittingly increasing the silica content of his enamels, obtains an insufficiently opaque product.

Natural cryolite occurs as a beautiful mineral in masses having a milky-white appearance; it is greasy to the touch, its specific gravity varies from 8·5 to 8·9, and its degree of hardness is 3. Cryolite may readily be scratched by the finger, crystallises in the monoclinic system, and is easily fusible.

The warning uttered in the case of felspar is still more necessary for natural cryolite, for it is always purchased in lumps and never as powder. Before use, the cryolite is carefully ground under personal supervision and mixed in a very finely powdered condition. Cryolite and its artificial substitutes act as fluxes, yet at the same time produce a more opaque enamel. In the preparation of white enamel the amount used must not exceed 15 per cent.

Ammonium Carbonate.—Many firms, when mixing their white enamels, add 3 to 4 per cent. of ammonium carbonate. Opinion as to the value of this varies enormously. On the one hand, the fact is put forward that ammonium carbonate volatilises on heating, and therefore its addition is pure waste, especially as the product is somewhat expensive. This is perfectly correct, with, however, certain reservations. On the other hand, it has been firmly established that the addition of ammonium carbonate to the enamel mixture has a favourable influence, since the action of the ammonium carbonate may be observed. The enamel is more uniform, and the so-called cracking (*Reifzen*) on firing is avoided. It is true that this actual result of experience still requires an explanation, for more than fifty years ago Moritz Vogelsang confirmed the observation in his interesting little work on *The Art of enamelling Iron* (*Die Eisenemaillierkunst*), and put forward the following explanation of the data obtained. He writes: "In all probability the effect of the ammonium carbonate may only be explained by cohesion, which force operates until the particular moment is attained at which the cracking (*Reifzen*) of the enamel ceases."

I gladly utilise the opportunity, as I now write about M. Vogelsang, to express half a century later my highest appreciation of his work—an appreciation which is rightly due to the man who nearly sixty years ago put forward, in his now antique little book, ideas and opinions which appear to me to be as full of valuable information as all the later and more recent publications. Vogelsang was the first writer who, from a scientific standpoint, gave us in a neat and concise form knowledge of the enamels and their raw materials.

Stannic Oxide.—This is an absolute necessity. Continual experiments, made with the object of replacing it by less expensive products, have without exception always resulted in a return to the original. At the present time it is almost exclusively added at the mill.

The ordinary method of preparation is by the gradual surface oxidation of perfectly pure tin in the blast furnace. 100 kilos. of tin yield 124-126 kilos. tin oxide.

Often small black specks are found in the enamel after covering and baking, which spoil the general appearance of the wares. These may be traced to dust, magnesia, etc., but in general they are caused by small specks of non-oxidised metallic tin, which may easily be present in imperfectly prepared stannic oxide. As soon as these imperfections are noticed the following investigation should be conducted:—

One kilo. stannic oxide is washed with water, or, more fully described, it is made into a paste and water allowed to run into it, accompanied by a vigorous stirring, periodically varied by being allowed to settle for about 10 seconds. The stannic oxide is carried away by the water, and the process of washing is continued, always more cautiously, until the decanted water appears clear. At the bottom of the vessel a grey, granular residue of metallic tin is left, which, being specifically heavier than the oxide, settles more quickly during the washing. This residue is collected, dried, and weighed, and the vendor who supplied it made answerable for the discrepancy. In many samples of stannic oxide the presence of up to 20 grammes of metallic tin per kilo. may be proved, *i.e.* 2 per cent.

During the manufacture of stannic oxide it may happen that particles of tin are only oxidised superficially, and inside may still be a nucleus of tin. In consequence of this the stannic oxide, where manufactured, is continually sieved and heated to redness in a special oven.

Different products, appearing on the market under diverse names, have been proposed as partial substitutes for the expensive stannic oxide, but a genuine success in this direction has yet to be recorded. The degree of opacity given by bone-ash or calcium phosphate is inadequate, while such a large amount of these substitutes must be added that the enamel is rendered absolutely useless. These facts caused me to try the antimony oxide derivatives, such as white antimony oxide, leukonin (potassium metantimoniate), etc., etc. The possibility of producing opacity by the above products is beyond question, yet we are met by the fact that their availability for use as an addition to the grinding is very restricted. If more than 4–5 per cent. be added to the mixture, the enamel will have its covering power diminished, and also be uneven and slimy. Still, however, antimony is the best partial substitute for replacing tin oxide.

As one is aware, the use of antimony and lead compounds in the preparation of enamels is forbidden in many countries, and this is the case in Germany and Austria-Hungary (the particular countries in which enamelled culinary utensils are manufactured). In the first place we have to bow before the authority of the law and avoid such compounds, while in the second place we are not able to take an independent position on the question of the use of antimony preparations as complete or partial substitutes for stannic oxide. And on this latter point we are involuntarily driven to the following train of thought :—The price of tin, as also of stannic oxide, is rising in alarming fashion, apart from the momentary unestablished speculative tendency, and stannic oxide has an important rôle in the expenditure of an enamel works. The price of raw material is increasing, wages are rising, and the selling price of enamelled goods is falling, or at the best of times remaining stationary.

Why is the use of products forbidden which give a somewhat better chance to the manufacturer of making headway against adverse market conditions, when civilised countries of the first rank, such as England, France, Belgium, America, etc.—models with regard to hygiene and other similar subjects—allow the use of antimony compounds ?

A really correct explanation would be difficult to give. It is said that antimony compounds are poisonous ; yet, granted that this may be the case, it is only true for soluble antimony compounds, and even then very large quantities are necessary in order to constitute a real danger to health. For example, an enamel contains 10 per cent. oxide of antimony, and a medium-sized cooking-pot of 5 litres content is enamelled inside with this enamel. For enamelling the interior of such a vessel about 100 grammes, say 120 grammes, of white enamel are necessary, and this would therefore contain 12 grammes antimony oxide. Now, antimony oxide is insoluble in water and very sparingly soluble in acids. Analyses have proved that on boiling for half an hour with 4 per cent. acetic acid no antimony has been dissolved, and even in particular cases where solution has taken place the amount dissolved was infinitesimal. Moreover, the antimony oxide in the enamel forms an insoluble compound with the silicates present.

Again, no mention has been made of any injurious action. In France, Belgium, etc., no single instance can be found, even of a case of very slight poisoning.

The danger due to antimony oxide in enamels is a fable as far as practice is concerned, like the famous, or infamous, romance of a French apothecary, who ascribed appendicitis (inflammation of the appendix) to the action of enamel splinters.

It matters not to us, who may enjoy, with a calm conscience, food which has been prepared in cooking-utensils coated with enamel containing antimony.

The fact that tin is becoming more and more scarce, and therefore more expensive, shows the need for a modification of the legislation by which antimony preparations are prohibited. Whether, indeed, much would be gained in the event of tin oxide being completely replaced by antimony compounds, remains to be seen. At present the enamel industry is one of the principal consumers of tin, and so soon as the demand for tin quite ceases the price must fall; while on the other hand that of antimony will materially rise, so that in such a case prudence and caution will be necessary.

Lead Oxide — Compounds.—Notwithstanding its valuable property as a flux, this is absolutely valueless in the form of calx (a mixture of tin and lead calcined) for producing opacity, on account of being detrimental to health. Our potters, by their wanton use of lead-glaze, have for generations caused mischief enough.

The gradual but successful supplanting of lead-glazed earthenware by the absolutely uninjurious, inexpensive, and more durable enamelled wares must, from the standpoint of hygienic economy, be regarded as an important advance. Here the objection could be raised against any restriction being made to the use of the beautiful, inexpensive lead-glaze for certain enamelled wares which are not concerned with the kitchen, such as sanitary articles, baths, door-plates, etc.

Theoretically, nothing could be said against it; but in practice, where in the same enamel works kitchen utensils and door-plates are made, the line of distinction between the different enamel preparations (those free from lead or those containing it) is not sharply drawn. An enamel containing lead, which at the outset may appear as beautiful as the rest, is unstable when exposed to weather, and at the present time it may safely be asserted that in no enamel works are lead preparations employed.

A simple experiment may be performed for the identification of traces of lead in an enamel.

A place on the enamelled object is spotted with a few drops of chemically pure nitric acid, and heated over a flame until the nitric acid is driven off, then moistened with distilled water and a few drops of a 10 per cent. solution of potassium iodide added. Traces of lead present cause an intense yellow discoloration, owing to the formation of lead iodide, which must be insoluble in ammonia.

While reviewing the bodies which produce opacity, our attention is involuntarily drawn to the well-known property which titanium oxide possesses of causing intense opacity in enamels. The initial product is rutile, a brown-coloured mineral, consisting of about 94 per cent. titanic acid and 6 per cent. iron oxide. The use of rutile for causing opaqueness only meets with strictly limited success, in the form of a maximum addition of 1 per cent. to the mixture, for the iron oxide present excludes all further use. For years a method has been sought of preparing chemically pure titanic acid from rutile, but the first products which appeared on the market years ago always possessed a faint yellowish-green colour and were expensive in addition, 1 kilo. of pure titanic acid costing as much as 15 marks (15s.). Many years back the firm of Wuppermann took out a patent for decolourising the enamels containing titanic acid; but the question remained a purely academic one, since it was not found possible to prepare inexpensively pure white titanic acid. Dr C. Dreper[*] a few years ago took out a patent in Freiberg. He prepared titanic acid by treating rutile with dilute sulphuric acid and sodium bisulphate, and then submitting the filtered solution to electrolysis. He placed the kathode in the filtered solution, and the anode in acidulated water, the liquids being separated by a porous cell, while the electrodes were of lead. A period of inactivity now took place until recently, when a method was patented by the chemical firm of Güstrow in Mecklenburg,[†] entitled "A process for the preparation of white opaque enamel and white opaque glass by the use of titanic acid as opacity-producing agent." The titanic acid prepared by this firm is pure white, and is moreover inexpensive, so that one can look forward to experimenting and gaining experience with it. The above firm has also introduced the barium salt of titanic acid to the trade, and this appears to be full of promise. This titanic acid may be added with advantage, up to 10 per cent., to an enamel during the grinding, and the enamel should be prepared as far as possible without saltpetre, but with the addition of 10 grms. of cobalt oxide to the mixture. Cases will arise in an enamel works requiring the closest attention for this material in order to discover the most suitable mode of employment. Titanium oxide appears to impart to the enamel favourable physical properties. An investigation should be made with the above to find out if the question of producing a lighter, more opaque ground-enamel is capable of a better solution, since the disturbing properties of tin oxide make these characteristics impossible.

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[*] D. R.-P. Nr. 152,257, Kl. 12*i*.

[†] D. R.-P. C. 15,243, Kl. 48*c*.

Cobalt Oxide.—This is one of the most ancient and precious of the ceramic colouring oxides. The intensity of the blue tint depends on the quantity present, and on the chemical composition of the respective cobalt oxides.

In the preparation of blue enamels more than 1 per cent. is seldom employed. On the market the following types are discriminated according to price and chemical composition :—

FHKO. The purest cobaltic oxide = Co_2O_3 containing 71 per cent. Co.
FKO. Pure cobaltic oxide = Co_2O_3 containing 60-65 per cent. Co.
RKO. Black cobalto-cobaltic oxide = Co_3O_4 containing 73 per cent. Co.
GKO. Dark grey cobaltous oxide = CoO.

KOH. Basic hydrated cobaltic sesqui-carbonate $= Co_5O_3(CO_3)_2 + 4H_2O$ containing 45 per cent. Co.

PKO. Red cobaltic phosphate $= Co_3(PO_4)_2 + 8H_2O$ containing 34 per cent. Co.

PO. Cobaltous oxide (protoxide) $= CoO$ containing 59 per cent. Co.

AKO. Cobaltic arsenate $= Co(AsO_4)_2 + 8H_2O$ containing 30 per cent. Co.

The value of the cobalt oxide depends upon the percentage content of metallic cobalt.

In order to make the best use of cobalt oxide for the manufacture of deep-blue enamels, a most intimate and continual mixing of the raw materials is necessary, so that the cobalt oxide is actually distributed as finely as possible throughout the enamel.

The most important of the pioneering countries engaged in the production of this valuable oxide are England and Germany.

Cobalt oxide possesses valuable physical characteristics which especially make it suitable for the preparation of ground-enamels, for these derive the property that their coefficients of expansion are as near as possible the same as sheet iron. The modern enamel firms, seeking to replace expensive materials by cheaper ones having the same influence, have replaced cobalt oxide with success in the ground-enamels by the much less expensive nickel oxide. The price-ratio of the two oxides is about as 10 : 1·2.

At this point a short theoretical diversion may be allowed to establish thoroughly by what quantities the cobalt oxide must be replaced by nickel oxide in a ground-enamel, so that the physical properties of the same may remain unaltered.

According to the law of P. Joubin, the product of the specific heat multiplied by the specific gravity of a body is proportional to the product of the modulus of elasticity and the coefficient of linear expansion of the specific heat = the quantity of heat, expressed in calories, which is necessary to raise a mass of 1 kilo. through 1° C.

Further, the product atomic heat multiplied by

$$\text{specific heat of unit volume} \times \left(\frac{\text{atomic volume}}{3}\right) = \left[\text{Melting point} \times \frac{(\text{specific heat of unit volume})}{1{\cdot}28}\right].$$

The specific heat = 0·1737 for iron.

For cobalt at 900° C. the specific heat is :

$$Sm = 0{\cdot}1444.$$

For nickel at 900° C :

$$Sm = 0{\cdot}13707.$$

Therefore, in order to raise 1 grm. of cobalt through 1° C., 0·1444 calories are required ; while to raise 1 grm. of nickel through the same range of temperature 0·13707 calories are needed.

Weber states that the requisite amount of heat necessary to raise a body from zero to its melting point (reckoned for the atomic weight) is inversely proportional to its coefficient of cubical expansion, and therefore the coefficient of cubical expansion for cobalt $= \frac{1}{0{\cdot}1444} = 6{\cdot}92$, while for nickel it is $\frac{1}{0{\cdot}13707} = 7{\cdot}29$.

From the ratio of the coefficient of cubical expansion of nickel to that of cobalt we have:

$$0{\cdot}1444 : 0{\cdot}13707 = 1{\cdot}052 \text{ grms.}$$

$$7{\cdot}29 : 6{\cdot}92 = x : 1$$

$$\therefore \quad x = \frac{7{\cdot}29}{6{\cdot}92} = 1{\cdot}053 \text{ grms.}$$

Concerning expansion, then, 1·053 grms. nickel will correspond for all practical purposes to 1 grm. of cobalt, or 100 grms. cobalt oxide may be replaced by 106 grms. nickel oxide in the preparation of a ground-enamel.

Limonite.—This in the pure state is manganese peroxide (MnO_2), but as a mineral it is known as pyrolusite. It is employed for decolourising white enamels which are discoloured. By the addition of larger quantities beautiful dark violet enamels are obtained, while iron oxide together with limonite produces lovely brown to black results. The limonite reacts by giving off oxygen, *i.e.* it is an ordinary oxidising agent.

Only the purest and best market samples are used, since the difference in price is trifling compared with the greatly enhanced results.

When fused in small quantities with the ground-enamel it works very favourably, and in like manner it is added to molten blue enamels in order to save cobalt oxide, for, as the cobalt content diminishes and the manganese addition is increased, the blue enamel takes a bluish-violet to reddish-blue glistening colour.

Ferric Oxide.—This is prepared by heating to redness protosulphate of iron or ferrous sulphate. According to the temperature employed, shades ranging from bright red to reddish violet are obtained.

The less the ferric oxide has been heated, the lighter will be the shade produced, so that great care must be exercised during the operation. More or less sulphuric acid is always present in the iron oxide, caused by incomplete decomposition, and therefore due to insufficient heating. On digesting with hot water, the bulk of the above may be removed, but this is the manufacturer's business. Insufficient heating of the iron oxide causes red enamel to be dull, and this, when stored as a finished product, acquires a permanent white efflorescence containing alkali sulphate. This white growth possesses a saline taste.

A qualitative test for free sulphuric acid, and also for the undecomposed sulphate in the ferric oxide, is easily made, viz.:—A few grammes of the ferric oxide compound to be tested are boiled with distilled water in a test tube, and after filtration a few drops of chemically pure hydrochloric acid are added to the filtrate. On the addition of a few cubic centimetres of a 10 per cent. barium chloride solution, the sulphuric acid is precipitated as barium sulphate, which is white. Should only a slight turbidity arise, then the iron oxide may safely be used.

Beautiful pure red iron oxide is formed when, to a boiling solution containing 17 parts soda to 68 water, 10 parts of crystallised ferrous sulphate are added gradually, the mixture being well stirred, then filtered, washed, allowed to oxidise in the air, spread in thin layers, and finally heated to redness.

The finest ferric oxide is prepared by the so-called method of Vogel, in which a saturated oxalic acid solution is added to boiling ferrous sulphate. The precipitate is washed and heated in a shallow dish at 200° C.

Other Colouring Matters.—Chromic oxide and also copper oxide are used for preparing green-coloured enamels. As regards chromic oxide the same remarks apply as in the case of ferric oxide. Cheap chromic oxide often gives dull enamels, accompanied by a separation of potassium dichromate. It is best prepared by heating potassium dichromate to redness; but if the chromic oxide obtained in this way has not been sufficiently heated and washed, a part of the potassium dichromate remains undecomposed, and separates out after the firing of the enamelled utensils.

The test made when purchasing chromic oxide is extremely simple, since only a few grammes of the oxide are treated with hot water, and the presence of undecomposed potassium dichromate demonstrated by a yellow-coloured filtrate. The amount of oxide added to the enamel mixture on grinding varies from 5 to 9 per cent. according to its quality and to the tint desired.

For lamp-shades, etc., a fused green enamel may be successfully prepared by melting enamel waste with 5 to 8 per cent. borax and 8 per cent. chromic oxide. The enamel waste has preferably been previously fused.

Chromic oxide may be prepared by another method, using 1 part potassium dichromate and 3 parts of burnt gypsum. This mixture is strongly heated to redness and then treated with very dilute hydrochloric acid. The following chemical reaction takes place:—

$$2K_2Cr_2O_7 + 2CaSO_4$$
$$= 2Cr_2O_3 + 2K_2SO_4 + 2CaO + 3O_2.$$

After boiling with dilute hydrochloric acid, whereby the lime goes into solution, the liquid is decanted off and the residue washed and dried. (A. Casali.)

Chromic oxide is also prepared by heating potassium dichromate to redness with flowers of sulphur. From 100 parts potassium dichromate and 50 of sulphur, 68 parts of chromic oxide are obtained.

The best chromic oxide is obtained by gradually heating ammonium bichromate, digesting with water, and then grinding. The lower the decomposition temperature, the more beautiful will be the green colour. Chromic oxide obtained by a wet method (solution of chrome alum + soda) is never so beautiful as when a dry process is used.

Cupric Oxide produces fine dark-green to bluish-green enamels, depending on whether the enamel contains saltpetre or not. The oxide must be fused with the enamel, as it is not suitable for addition on grinding, in consequence of its exceptional behaviour.

The reducing gases in the muffle may in the case of enamels prepared from cupric oxide bring about a separation of copper in the form of faint red spots.

Coloured substances varying from green to bluish violet are obtained, according to Le Chatelier,* from: 30 parts silica + 49 parts heavy spar ($BaCO_3$) + 20 parts cupric oxide, heated for an hour at 1050° C. The shade obtained is bluish violet. Or: 375 parts silica + 265 parts heavy spar + 7 parts cuprous oxide + 42 parts sodium bicarbonate. This mixture, heated to 1200° C., gives a pure blue.

A Bluish-green Oxide is prepared from copper and cobalt salts, or with chromium and cobalt salts. According as one or the other of the oxides prevails, bluish-green to greenish-blue shades are produced. Reviewing the price-list for the green and blue colouring oxides, a bluish-green or Turkish-blue oxide will be cheaper as the colour inclines towards the green, and more expensive when towards the blue. At the mill ½–1 per cent. is added according to the desired

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[*] D. R.-P. Nr. 112,761, 11th October 1899.

shade. Since this blue-green oxide is one of the most expensive, and therefore most in demand, lighter shades of blue-green enamels are recommended for use, these being moreover much more delicate and elegant than the richly coloured and expensive blue-green enamels.

The yellow enamels are usually prepared by adding cadmium, chromium, or uranium salts when grinding. Cadmium sulphide gives very beautiful colours, also lead chromate, but its use is avoided as far as possible, on account of the lead content. Uranium salts and barium chromate are seldom employed.

Brown Colouring Matters.—Brongniart's brown is a very beautiful brown colouring matter, consisting of ferrous chromite. It is prepared by adding a solution of potassium chromate (1 in 3) gradually to one of pure ferrous sulphate (1 in 3). The precipitate is washed six times, dried, and heated to redness in a crucible, then finely powdered.

Rose Colouring Matters.—The rose-coloured enamels are prepared by colouring with gold salts; usually, however, by the addition on grinding of 6–10 per cent. of the so-called pink-rose.

It is difficult to obtain the same shade on all occasions, since after preparing and firing the pink-rose changes in shade and colour intensity. The enamels which have been coloured by the above are very unstable against fire. Also every place on the enamelled utensil which has been touched by the perspiring fingers of the workmen remains white, in consequence of the reduction which sets in.

What concerns the preparation of the pink-rose substances applies also to the mixture of chalk, quartz, tin oxide, borax, and potassium dichromate, which is heated to redness, the dye-stuff so obtained being digested with water, levigated, and washed. The preparation of pink-rose by this particular method is not recommended, on account of the inherent difficulties. Pink-rose (*Pinkrosa*) is counted among the most antique of the ceramic colours, the name being suggested by the English term "pink colours" (*Nelkenfarbe*). The exact chemical composition has not up to the present been fixed, but it appears to be a stannate or a chromium and calcium salt of stannic acid.

A very useful mixture for its preparation is afforded by: 50 kilos. stannic oxide, 25 kg. chalk, 18 kg. quartz, 4 kg. potassium dichromate, and 6 kg. borax.

The rose colour prepared by employing gold salts is only used for fine artistic enamels, and is distinguished from the other similar colours by its stability against fire.

Purple (Purple of Cassius), a ceramic colour for making intense purple-coloured glazes, was well known to the ancients, being the most expensive and the loveliest red which is used in the ceramic and enamel industries. It is therefore only employed for decorating the better-class utensils.

Purple of Cassius * is prepared by the addition of 1 part auric chloride to a solution containing 1 part of stannous chloride and 2 parts stannic chloride, when a purple-red precipitate is formed, which is collected, washed, and dried.

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* Cassius, inventor of gold-purple, 1683, in Leyden

If instead of 1 part gold chloride only half a part is taken, and the other half replaced by a silver salt, a beautiful carmine red is produced.

The true chemical constitution is not yet clear. It is regarded as a lake of metastannic acid coloured by finely divided gold (Debray).*

Moissan,† the famous French chemist to whom we owe calcium carbide and other valuable discoveries, was occupied with this question shortly before his decease. He pointed out the remarkable fact that from the gold-purple obtained he could evaporate gold at the temperature of the electric furnace. Moissan tried the same experiment with an alloy of gold and tin, and found that, as the tin more quickly evaporated, a purple vapour formed, which was deposited in powdered form in the furnace. He obtained different varieties of purple, according as gold was used in the presence of aluminium, magnesium, zirconium, or silicon. This experiment confirms the view put forward by Debray for the constitution of gold-purple.

Gold Glance.—This is an indispensable requisite for decorating enamelled wares. It is best procured in large bottles, from which a definite amount is weighed out daily into a small work-vessel and given to the artists. On account of the unavoidable loss, the import in smaller bottles is inadvisable. Gold glance is prepared by dissolving auric chloride (gold dissolved in aqua regia, the mixture evaporated, and the residue dissolved in water) in a little water and adding 8–9 parts of a mixture of sulphur balsam in lavender oil (4 parts sulphur balsam and 4 parts lavender oil). The contents are vigorously stirred with a pestle, and allowed to stand twenty-four hours, in order that all the evolved hydrochloric acid due to mixing may escape. Usually half a part of finely powdered basic bismuth nitrate is then added, and the mixture allowed to stand again. By this means the gold will be made to adhere better. In all probability the following chemical reaction takes place :—

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* Debray, *Comptes rendus*, lxxv., p. 1025, 1872.

† *Bulletin de la Société Chimique*, 1906, p. 267.

$$3C_{10}H_7S + AuCl_3 = C_{30}H_{18}S_3 + 3HCl + Au$$

(sulphur balsam).

This is the process of Dutertre.

It is important to collect together all the waste materials from the gold glance process, such as the artists' overalls, brushes, glass plates and bottles, for the recovery of the gold. Gold glance contains about 10-12 per cent. gold. The above mentioned articles are placed in a pot and burnt in the muffle. The empty bottles are likewise heated, splintered by water, and the glass powdered. The ash and glass fragments are then placed in a sufficiently large porcelain dish, aqua regia added, and the whole evaporated on the water-bath until the odour of nitric acid disappears. After cooling, aqua regia is once more added, and again evaporated until the evolution of fumes ceases. Hot water is then added, the whole being well stirred and filtered. The gold goes into solution as auric chloride, to which a freshly prepared solution of the purest ferrous sulphate ($FeSO_4,7H_2O$) is added gradually, whereby the gold separates in the form of a yellowish-brown metallic powder, which is filtered, washed, and dried.

In many works the loss of gold glance is often considerable, and this alone is a sufficient recommendation in the majority of instances for the recovery of the gold from the waste materials. Many firms utilise the empty bottles which have held the gold glance for the preparation of rose-coloured enamels. The bottles are heated to redness, splintered, the glass powdered and added in the proper proportions to a mixture of white enamel in the smelting furnace.

Lustrous colours are seldom used, on account of their high price; but whether in the future the production of lustrous enamels will catch the popular eye remains to be seen. One or two metallic lustres are already prepared in large quantities, and there is no reason why, in the case of enamels, similar plays of colour should not be prepared chemically as in glass and porcelain manufacture. There is no lack of recipes and formulæ, but the times and demand are not yet ripe.

For the sake of curiosity, some of the above-mentioned recipes may be noticed, as they have been used in part by the Arabs for preparing metallic reflections on artistic enamels.

A mixture of copper and silver carbonates $(95CuCO_3 + 5Ag_2CO_3)$, or 30 per cent. copper carbonate and 70 per cent. red ochre, or 20 per cent. copper sulphate, 25 per cent. stannous oxide, and 55 per cent. red ochre, were well powdered in the presence of a little gum arabic, finely triturated with water, and added to the transparent enamels; the wares being fired at 900° C., allowed to cool, and again heated in the reducing fire at only 650° C. In this way very beautiful effects have been obtained.

L. Tranchet (*Comptes rendus*, 1905, pp. 1020 et 1237) gives several other formulæ :—

(1)	Enamel A	100·0
	Kaolin	10·0
	Silver carbonate	2·0
(2)	Enamel or substance A	100·0
	Kaolin	10·0
	Zinc oxide	1·0
	Tin oxide	1·0
	Silver carbonate	0·5
	Copper oxide	3·0
(3)	Substance A	100·0
	Kaolin	10·0
	Bismuth subnitrate	4·0
	Silver carbonate	2·0
	Copper carbonate	1·0

The substance A had the following composition:—

Quartz	12·0
Felspar	10·0
Kaolin	2·0
Sand	20·0
Minium (red lead)	30·0
Borax	19·0
Boric acid	2·0
Potash	2·0
Common salt	1·8

The substance A was fused, splintered by water, and ground at the mill, temperature 970° C.

	Arabian Formula.	Italian Formula.
Copper sulphide	26·87	24·74
Silver sulphide	1·45	1·03
Red ochre	71·98	49·45
Mercuric sulphide	...	24·74

When firing the wares, the so-called green broom (German *Pfriemenkraut*, French *Genêt vert*, also Spanish *Klepper*) is placed in the interior of the muffle for combustion.

This slight deviation may be excused on the ground that one should not stand aloof with regard to hints and statements in the literature. If the question of the production of metallic reflection on enamels by using artificial lustrous colours is not at the present moment acute, yet a demand for the same may arise at any time. These formulæ are not easily obtainable, and are quickly forgotten.

Clay and Kaolin.—I have omitted to mention a material so important to the enamel industry as clay. At first sight there is apparently not much to say, yet in reality many volumes might be written on clay and its position in our industry.

And this is indeed an error which many enamel firms commit, viz. that they do not pay suitable attention to their clay; and many of the mistakes which have been explained away in the most impossible and fantastic ways have their origin here.

Chemically, we understand by clay and kaolin a compound of alumina and silicic acid, contaminated by more or less lime, magnesia, etc., according to its origin.

Clay has been originally formed by the decomposition of the felspars. Where the latter were to be found thousands of years ago, they have been gradually decomposed by the influence of the atmosphere, carbonic acid, water, etc. The water takes up the compounds of silicic acid with the alkalies, deposits them elsewhere, and leaves behind the insoluble compound of silicic acid with alumina, viz. clay.

If the clay still remains in its original situation, we term it kaolin; but should the clay after formation have been gradually transported by water and deposited elsewhere, then we speak of ordinary clay.

Kaolin, then, is residual clay, as distinguished from the ordinary variety which has suffered transportation. We must look, then, for kaolin among the primitive rocks, since it is older than ordinary clay. An ideal clay would consist of :—

45 per cent. alumina or aluminium oxide.
40 „ silica or quartz.
15 „ water of composition.

In nature the composition varies, the so-called standard clays being presented in the following table :—

ANALYSES OF STANDARD CLAYS.

	Ia. Clay from [illegible] Pit [illegible] Clay		Zettlitz Kaolin		Belgian Clay from the Ardennes.		[illegible] Clay from M[illegible] near Coblenz		[illegible] Ia Clay similar to K[illegible] from a Secondary Position.		Ober-aufungen. Moderate Lignite Clay.		Niederpleuz Inferior Lignite Clay	
Alumina .	30·30		3[illegible]		[illegible]1·73		[illegible]		35·05		27·97		28·05	
Silica as sand	[illegible] [illegible]·90	4[illegible]	[illegible] [illegible]·15	45·[illegible]	40·[illegible] 9·95	49·[illegible]	41·00 6·71	47·74	39·32 8·01	47·33	33·59 24·40	57·99	30·71 27·61	58·32
Magnesia . .	0·19		[illegible]		0·41		0·33		1·11		0·54		0·75	
Lime . .	[illegible]·10		0·0[illegible]		0·18		0·40		0·16		0·97		0·72	
Iron oxide . .	0·[illegible]0		[illegible]·00		1·80		2·57		2·30		2·01		1·89	
Potash . . .	0·42		0·00		0·41		1·05		3·18		0·53		1·39	
Loss when heated to redness . .	17·78		13·00		12·00		11·[illegible]		10·51		9·43		8·66	
Fireproof . .	100		60-70		50		45		30		20		10	
	poor		poor		very rich		rich		very rich		very rich		very rich	

For enamelling purposes a good white clay containing about 36 per cent. alumina and 40 per cent. silica is preferable to kaolin ; for the latter, notwithstanding its purity, does not give in most cases that degree of expansion to the enamel which is essential. Localities for finding really good enamelling clay are becoming more scarce. The best varieties come from the Rhine neighbourhood, near Coblenz (Vallendar), and the Ahr valley, in the region of Bad Neuenahr. The clay from Sauerland possesses valuable properties similar to that of Vallendar. Unfortunately, these pits are now exhausted, and the opening of new deposits must be continually taken in hand.

The treatment of clay in the enamel works before its use as an addition to the enamel requires careful and conscientious attention. The following may be stated, not in the sense of revealing secret operations, but in order to remind every expert anew of the value attached to the conscientious preliminary treatment of the clay.

The clay, before use, must be soaked as thoroughly as possible for two, or at least one day, in pure water at the temperature of the room. Since clay always contains enclosed organic matter of a vegetable or other origin, this must be removed; and therefore a weak fermentation is induced by soaking in water, which continues unaided if the mixture is allowed to remain at a moderate temperature. After a suitable time has elapsed, the clay is boiled with water for a short period, in order to terminate quickly the fermentation, and to drive away the last of the gaseous products so formed, such as carbonic acid.

The clay is then passed through a fine-meshed enamel sieve, using as much water as possible, allowed to settle, the water decanted off, and the clay thus prepared added in requisite amount to the enamel when grinding. Usually the quantity added varies between 5 and 10 per cent., sometimes reaching 12 per cent.

Should a clay contain an especially large amount of organic matter, and this be added to the enamel without undergoing the treatment described above, in particular without being boiled, small blisters frequently arise in the enamel. These blisters are caused by the carbonic acid contained in the fermenting clay.

How much annoyance may be spared by careful treatment of the clay! and, on the other hand, how many mishaps are due to badly controlled enamel mills!

A Short Note on Water.—An important factor, on which success depends, is water. On principle, the purest water should be used for grinding enamel in the wet way. The most ideal kind is rain water or melted snow; but these, unfortunately, are not always at disposal in sufficient quantity, so that well or river water must be used.

The use of very soft water which has stood for some time is especially recommended. Where soft water is not at hand, a little pure milk of lime is added to hard water, the mixture thoroughly stirred and allowed to settle over-night for use on the following day. This treatment of the water has a particularly good influence on ground-enamels. Condensed water may not be so pure as alleged; water which has filtered through land, and pond water, must absolutely be avoided. A chemical analysis of the water regularly used at the mill should be made three or four times a year.

In general, for water of good quality the following data may be accepted: 1 litre of water may contain:—

Chlorine	less than 0·015 grm.
Sulphuric acid	0·002–0·005 ,,
Organic matter	less than 0·001 ,,
Volatile ,,	,, 0·015 ,,
Total hardness	2–8
Hardness after boiling	1–3

It is often important to be able to test quickly and simply for the presence of chlorine and sulphuric acid in cases where one suspects the water used in the enamel mill to be contaminated by the waste water from the cleansing process. The procedure is as follows:—

Test for Traces of Hydrochloric Acid in Water.—A small sample of the water is placed in a clean test-tube, 2 drops of pure dilute nitric acid and a few drops of dilute silver nitrate solution added (5 grm. silver nitrate dissolved in 100 grm. distilled water). If chlorine is present, a white turbidity, and often a heavier white precipitate, is obtained, due to the formation of silver chloride. The amount of turbidity will afford an estimate of the quantity of chlorine present. A faint translucent turbidity is often unimportant. The precipitate of silver chloride must dissolve in ammonia.

Test for Traces of Sulphuric Acid in Water.—A small quantity (10 c.cm.) of the water to be tested is placed in a test-tube, 2 drops of dilute nitric acid and a few cubic centimetres of a dilute solution of barium chloride (10 grm. barium chloride dissolved in 100 grm. distilled water) added. The presence of sulphuric acid or its salts is detected by a more or less thick white turbidity, or, if a large amount of sulphuric acid is present, a white precipitate of barium sulphate forms. The chemical reagents necessary are furnished by every apothecary or druggist.

Coal.—A few remarks may be made on this necessary combustible for the production of the temperature required for fusion in the enamel-smelting furnace and in the muffle. As the consumption of coal is extraordinarily great, many enamel works have been erected in the neighbourhood of coalfields. The amount of coal required for firing completely 100 kg. of enamelled wares may be taken as 120 to 250 kg., according to the construction of the furnace, mode of firing, quality of the coal, and, last but not least, according to the activity of the workers. The coal consumption is directly connected with the mode of heating the muffle. In Saxony and Bohemia, where the best quality of lignite (up to 6000 calories) may be obtained cheaply, it is used in the enamel works.

Austria possesses good pit-coal in the Ostrau-Karwiner district and in the Pilsen basin. Hungary's pit-coal and lignite are of less value, and leave up to 25 per cent. residue. Most of the coal used in the German, French, and Swiss enamel works is imported from Westphalia. Some data of German standard coals may be inserted here.

	Name of the Pit.			
	Count Bismarck.	Hardenberg.	Schlagel u. Eisen (Iron).	North Star (Nord-stern).
Weight of 1 cubic metre	696	741	700	741
Cohesion in percentage	83	77	78	83
Unused residue	4·24	5·94	3·6	9·00
Water evaporated from or reckoned in kg. from 100 kg. coal	7·21	7·3	6·88	6·72

Lignite usually contains:—

Carbon	44–57 per cent.
Hydrogen	1·9–2·8 „
Water	35–47 „
Ash	5·0–7·5 „
Calories	3500–6000

Pit-coal usually contains:—

Carbon	70–80 per cent.
Hydrogen	3–4 „
Water	13–23 „
Ash	3 „
Calories	6600–8000

The large water-content causes the carriage of lignite to be unprofitable, especially where no inexpensive means of water-transport is to hand.

Lignite should never be stacked higher than 1·5 m., on account of spontaneous combustion. Pit-coal may be piled up a little higher.

AVERAGE COMPOSITION AND VALUE OF SOME BRITISH FUELS.

Description.	C	H	O	S	Ash, including Nitrogen.	Total Heat of Combustion.
Welsh . .	83·87	4·79	4·15	1·43	5·89	14858
Newcastle .	82·12	5·31	5·69	1·24	5·12	14820
Derbyshire .	79·68	4·94	10·28	1·01	4·06	13860
S. Yorkshire	81·88	4·83	7·47	·54	2·95	14296
Lancashire .	77·90	5·32	9·53	1·44	0·18	13918
Scotch .	78·53	5·61	[illegible]	1·11	5·03	14164
Irish Anthracite	80·03	2·30	...	0·76	11·03	13302
Coke (Durham)	88 to 92	...	...	·25 to 2·0	4 to 12	12832

Too large storage of coal must be avoided, since the coal, after being stacked a long time, falls to pieces, accompanied by a partial evolution of gas, causing deterioration thereby. In many cases it is advisable to sprinkle the surface of the pit-coal with water previous to burning, whereby a loss of unconsumed coal-dust will be avoided.

The necessity for a thorough and regular control of the coal entry and exit cannot be too strongly recommended, the latter being exactly recorded for each separate firing. The heating itself requires extremely great care, strenuous work, and undivided control. Something will be said concerning gas analysis in the chapter entitled "Firing of the Enamelled Utensils."

The last, but none the less important, materials in our industry of enamelling on sheet and cast metals are the latter metals themselves.

Sheet and Cast Iron.—For the preparation of a faultless enamelled ware, one of the most important items is faultless sheet metal or a flawless casting, possessing a definite chemical and physical behaviour.

Almost exclusively at present a soft sheet steel is used, *i.e.* rolled-out steel which has been prepared according to the basic Martin process in the special Martin furnace. For utensils which have not been forged, but only made up from sheet, and where, therefore, nothing has been exacted from the physical properties of the steel, the somewhat less expensive and more simply treated sheet steel is used.

The quality of the steel is unfortunately often variable, and dependent on the care exercised during its manufacture at the iron-works. Good forged sheet steel should be box-heated, a term derived from the process of heating in iron boxes, as far as possible with the exclusion of air. Often impurities, such as particles of slag, etc., will be rolled in with the sheet metal, so that on forging, and even more on enamelling, flaws will develop in wares prepared from such material. Chemically, a well-forged sheet for enamelling purposes should possess the following composition:—

Carbon . . .	0·050–0·080 per cent.
Manganese . .	0·230–0·350
Phosphorus . .	0·002–0·080

and, at the most, traces of silicon.

Regarded physically, it should possess the following coefficients

Coefficient of tenacity	35–38	per cent.
„ contraction	56–65	„
„ elasticity	30–38	„
Specific gravity	7·6–7·8	

The immediate analysis of the purchased metal, so as to buy it on the basis of the previous figures, is most strongly recommended. The physical examination is carried out by the testing-machine, the purchase of which is advisable, on account of the quicker and more simple investigation of the sheet metal. This machine is based on the principle of the decimal balance, in which the sample strip to be broken is stretched in position on the beam between two levers, and on adding to the load by placing weights on the scale an increasing tension is obtained until finally the sample breaks.

England and Germany produce most of the forged metal, and the larger part of this of first-rate quality. In addition, Austria-Hungary and France manufacture good forged metals in several iron-works, but these are frequently expensive. Moreover, the adaptability of these works is often very limited.

Austria-Hungary grants to enamel firms the rebate of the tax on English or German sheet metals in the case of exportation of the enamelled wares prepared from them. In consequence of this it is possible to employ first-class English sheet-iron in the manufacture of wares for export.

Until the year 1896, almost all the forged metal used in the German enamel works was imported from England. The annual consumption of metal for enamelling purposes is estimated by Dr H. Wuppermann at 70,000 to 85,000 tons, having an approximate value of £1,000,000. The data giving the decrease in the import may be directly applied to the weight of the quantity of enamels used. Here may be mentioned the more complete statistical treatise of Dr Hermann Wuppermann, *The Sheet Metal Enamelling Industry in Germany.*

The tax levied in Germany for imported sheet metals, according to the customs tariff of 25th December 1902, for pieces more than 1 mm. thick, amounts to 30s. per ton, and for thicknesses of 1 mm. or under, 46s. per ton. For rolls the tax is raised 25 per cent.

In the case of foreign metals, rolls are recommended, the saving in freight being 50 per cent.

The most thorough management of the metallic stock is indispensable, and is greatly facilitated by having a specially designed storehouse, where the sheets may be stacked according to size and thickness. It is self-evident that such a store should be kept dry, to prevent the metals rusting. The utilisation of the metal to the best advantage by cutting out the shape to be folded for the crude ware, or the preparation of rolls, should be as economical as possible. The larger metallic fragments may be profitably used for the manufacture of hollow handles, knobs, children's toys, etc.

A frequent, and if possible daily, oversight of the metallic fragments is an indispensable duty of the official entrusted with the management, for many a badly forged article, often due to the workmen, will be exposed by an efficient control.

Cast Iron suitable for Enamelling Purposes (*Cast Iron for Utensils or Pots*).—If not exactly within the scope of the industry concerned with sheet metal enamelling, yet the importance of the manufacture of enamelled cast-iron wares for special purposes, such as the preparation of hygienic implements, water-closet appliances, water-pipes, baths, basins, etc., and often for cooking-vessels, chemical apparatus, etc., should not be underestimated.

Corresponding to the essential chemical and physical difference between sheet and cast iron is the treatment and preparation of the enamels, etc., which for the enamelling of cast-iron vessels differ from those in the process of enamelling on sheet metal. The iron suitable for pots and utensils is a thin wrought iron, which gives a sharp mould, and possesses a smooth surface; and for this purpose the inexpensive pig-iron containing phosphorus, with a little manganese and a moderate silicon content, is suitable (prepared from bog-iron ore, which earlier was regarded as valueless), since a certain amount of brittleness or a somewhat lower strength does not matter.

The English quality corresponding to the above is found near Middlesborough, and the German variety, the so-called Lorraine or Luxembourg pig-iron, near Luxembourg.

English pig-iron contains :—

Carbon	3·5	per cent.
Silicon	2·0	„
Phosphorus	1·4	„
Manganese	0·7	„

Luxembourg pig-iron contains :—

Carbon	3·6	per cent.
Silicon	2·0	„
Phosphorus	1·8	„
Manganese	0·5	„

For thin objects, which, in consequence of rapid cooling, are more brittle than thicker ones, the property of phosphorus in producing this brittleness is inconvenient, and in the case of a high phosphorus content a little more silicon serves as a remedy. To the above pig-iron 40–50 per cent. of good bog-iron is added.

For thin hardware, which easily becomes brittle, the use of a more tenacious iron containing increased quantities of silicon and carbon is recommended, so as to acquire a more uniform, smooth, blue surface; the better German and English varieties are therefore prepared with the addition of 1–2 per cent. of steel (fragments from the Bessemer process, which, however, must not be rusted over), or pieces of wrought iron, to the molten metal. This small addition of steel is often made with advantage at the foundry. Steel in contact with the glowing coke of the cupola furnace takes up carbon and changes into grey pig-iron, providing the silicon content of the molten metallic mixture is sufficient.

Arsenic, antimony, copper, or chromium should not be present, even in small quantities, in the cast iron. If P is the weight of the mould, then the weight of the cast iron is approximately, for moulds of—

Pine or fir-wood . .	14·00 × P
Oak	9·00 × P
Beech	10·00 × P
Lime . . .	13·50 × P
Birch	11·00 × P
Alder	13·00 × P
Brass	0·90 × P
Zinc	0·80 × P
Lead	0·70 × P
Cast iron . . .	0·97 × P

Difficulties in the process of enamelling hardware are frequently caused by adhering mould-sand which has been burnt in. To avoid this, [illegible] per cent. of powdered coal is mixed with the sand, and the inside of the mould is sprinkled with charcoal dust. Before etching the hardware, it must be carefully cleaned by wire brushes, files, etc., so that finally, with the aid of the sand-blast, a metallic surface suitable for etching and enamelling will be obtained.

CHAPTER III.

THE PREPARATION OF THE ENAMEL.

THE mixing of the enamel, *i.e.* the intermingling of all the raw materials the object of which, after fusion, is the finished product, is carried out in a special chamber. Since the preparation of enamel is a trade secret, the mixing is performed in small firms by the owner himself or his representative, while in larger establishments, where the daily enamel production is on a scale too vast for the owner or manager to deal with exclusively, the following procedure takes place :—

The official entrusted with the preparation of the enamel mixes together the smaller constituents, such as soda, saltpetre, cobalt-nickel oxide, magnesia, braunstein, and in addition a small part of the borax, felspar, and cryolite required in the formulæ described earlier. The workman takes from this preliminary mixture the corresponding quantity, and completes the mixture by adding the materials in the amounts given him. A small example will serve to illustrate.

A formula for white enamel runs as follows :—

Borax	132 kg.
Quartz	152 "
Felspar	130 "
Soda	26 "
Saltpetre	6 "
Cryolite	78 "
Fluorspar	3 "
Magnesia	6 "
Total	533 kg.

This is subdivided as follows :—

	Mixture by	
	The Official in Charge.	The Workman.
Borax	12 kg.	120 kg.
Quartz	12 "	140 "
Felspar	30 "	100 "
Soda	10 "	16 "
Saltpetre	6 "	...
Cryolite	28 "	50 kg.
Fluorspar	3 "	...
Magnesia	6 "	...
Total	107 kg.	426 kg.

That only very trustworthy workmen should be entrusted with the mixing operation, will be self-evident.

As already mentioned, the raw materials to be mixed must be as dry and finely powdered as possible, for then the mixture will be more intimate, and in consequence the fused enamel more uniform. In the larger works a practical balance with the mixing boxes placed upon it is fitted up. The mixing chamber should be well ventilated, and during the process any unnecessary production of dust, involving loss of material, must be avoided. The pot or metal chest in which the finished mixture is transported to the smelting furnace should always be thoroughly cleansed, while in the case of blue and ground enamels separate boxes are to be preferred. The more expensive metallic oxides should be separately weighed on small balances. Cobalt oxide requires an especially long time for mixing, so that the colour intensity may be properly developed.

With smaller quantities (up to 200 kg.) the mixing is performed by a workman who employs a crook for the purpose, but larger quantities are brought together by a mechanical mixing apparatus or mixing cylinder. Careful mixing by hand is, however, more reliable. The rule may be stated that the smaller the quantities taken the more intimate the mixture. Larger quantities, up to 800 kg., which are mixed in the "melangeur," must remain a correspondingly long period in the apparatus—in fact, up to thirty minutes. Coloured enamels require an especially long time.

The crude enamel mixture must be put through a wire sieve (width of meshes 5 to 7 mm.).

The saltpetre usually gathers into small balls, which must be carefully crushed by hand.

In a well-conducted works, stress will be laid on the exact manipulation of the blended raw materials which when fused together form the enamel, on the one hand to ascertain precisely the loss on melting and therefore the value of the enamel, and on the other to expose negligence.

Above all, the balance should play an important part in the enamel industry. All the materials which enter and leave, whether proceeding from the mixing chamber, or leaving the furnace, or entering the mill, the enamel from the latter, coal, the etched ware, etc., all are weighed, and a really efficient service at the balance renders most valuable help to the works management.

The Melting Process. — From the mixing chamber the enamel proceeds to the melting furnace, which is generally a blast furnace (*Wannenöfen*) and seldom a crucible furnace. According to the dimensions of the workings, the furnaces are provided direct with 50 per cent. gas or generative heating.

The crucible furnace gives very good results in the case of the best enamels, but its utility is limited and the cost of maintenance too great, so that at present the blast furnace is almost exclusively used. The dimensions of the latter must not be too great, but correspond to the proportions of the melt.

What was stated with regard to blending finds its parallel here. The smaller the portions, the more uniform the fusion and the finer the enamel.

In works of moderate size the charge should not exceed 150-200 kg. at any single operation.

Larger works are necessary, however, in consequence of the large consumption, and these must be able to deal with over 200 kg. at a time. If the temperature of the furnace is insufficient, then the charge of enamel must remain there longer, doubtless to the detriment of the product, for not only discoloration but frequently a decomposition of the enamel may set in. Moreover, every expert knows the disagreeable consequences of working with an under-fused enamel.

Too high a temperature in the furnace is in a like manner objectionable, since combustion of the enamel may take place, or a premature decomposition of the separate materials may proceed before the mixture has time to unite chemically to form a silicate. The mean temperature lies between 1100 and 1200 C.

Special emphasis is laid on a very vigorous crooking, viz. stirring the molten enamel in the furnace by means of iron crooks.

Success depends largely on this latter operation. On melting the enamels there commences a distinct separation of the constituents, according to their specific gravity. The borax, soda, and cryolite melt, while the fusible quartz and felspar endeavour to settle to the bottom Should frequent and conscientious stirring be neglected, there develops an uneven exclusion of the silicate, with consequent deterioration in the quality of the enamel. The duration of the fusion may be taken as two hours for white, and two and a half to three hours for ground and blue enamels The latter should be vigorously fused, but this must be abated for white enamel before complete devitrification takes place, otherwise it will become more transparent and less opaque. From time to time samples are taken from the furnace with an iron bar, and should the glass threads of enamel which form exhibit the partial development of knots, then the enamel must remain longer in the furnace.

In addition, before drawing off the enamel, a small specimen is placed in a vessel, allowed to cool, and the fractured surface observed. Well-fused enamel shows a bright, absolutely smooth surface, and fracture free from porosity.

Many of the smaller works fill the furnace with the mixture to be fused, and allow the molten enamel to run off continuously, while the mixed materials are persistently added to the furnace.

That this form of continuous working is not suitable follows from the reasons offered above. On fusion two factors operate in causing a loss of enamel: on the one hand the decomposition of certain constituents, which give off their water of crystallisation or carbon dioxide (borax 47 per cent., soda 41 per cent., since only calcined soda is used, saltpetre 61 per cent.), and by the partial loss of hydrofluoric acid from the cryolite and fluorspar; on the other hand there is the loss in manipulation, which ordinarily should not exceed 3 per cent. The average total loss on fusion may be taken at 15–23 per cent. An estimate should be made for each separate case, in order to show what amount of enamel may be obtained by suitable manipulation of the raw materials.

The molten enamel is allowed to run into cold water, in order to splinter it, the water then being run off and the moist enamel either taken direct to the mill or to the storehouse. Many firms dry the fused enamel, but the majority use or retain it in the moist condition as it comes from the water chambers attached to the furnace. In the latter case the enamel contains about 4 per cent. of adhering moisture, which must be taken into account when estimating its weight. For storing the fused enamel, chambers are used which are protected against wind, rain, and dust, the floors being cemented and the side walls covered with sheet zinc.

Separate compartments are employed for the different varieties of enamel, which must be maintained in a condition of the utmost cleanliness.

As an example of the calculations whereby the loss during fusion is arrived at, the following composition of a ground enamel will serve:—

[redacted]	72·0	kg.,	loss 47 per cent. =	33·80 kg.
Felspar	55·8	,,	...	...
Quartz	31·2	,,	...	...
Soda	8·4	,,	loss 41 per cent.	3·44 kg.
Fluorspar	7·2	,,	...	...
Saltpetre	5·4	,,	loss 61 per cent. =	3·29 kg.
Cobalt oxide	0·4	,,	...	...
Limonite	1·2	,,	loss 9 per cent.	0·11 kg.
Total	181·6 kg.		Loss =	40·64 kg.

181·6 kg. of mixed ground enamel give, according to the mode of fusion, 181·6 – 40·64 = 140·96 kg. of fused enamel. This gives a loss on fusion of 22 per cent., to which must be added a still further loss of about 2–3 per cent. due to manipulation.

The Grinding Process.—The fused enamel is taken to the mill, where it is ground in stone mills (with nether millstone and adjustable bearings) or drum mills. The latter are not suitable for the moist grinding of white enamel, but may be employed with advantage for large quantities of coloured enamels. The fact is that white enamel ground by stone mills is not only finer, but also more opaque, for the particles of tin oxide appear to be crushed and distributed better throughout the enamel by grinding in this way.

In the grinding room the most scrupulous cleanliness is observed, and the production of dust avoided. The amount of fused enamel to be ground varies from 20–40 kg., while the duration of the process will be, according to the quality of the enamel and the grade of fineness desired, between four and twelve hours. Water is added up to 30 per cent. for white, and 40 per cent. for ground-enamel, of the weight of the portion taken. Since during the grinding operation loss of water may frequently occur, care is always taken to replace this; otherwise, in consequence of friction between enamel and millstone, heat may be evolved and thereby the quality of the powder unfavourably influenced. In such cases the enamel is said to be burnt (*verbrannt*), *i.e.* it loses its lustre when burnt into the utensil

The deterioration of the enamel so caused is traced to a loss of lustre consequent on overheated mill-stones.

Certain compounds are added to the moist grinding, not only to develop the white, red, or green colour, but also to make the enamel capable of use for the subsequent enamelling of the crude ware. Fused enamel, ground without these additions, would be useless, as it would quickly settle to the bottom.

As additions on grinding there are used: stannic oxide for developing an intensive white in the enamel; such colour oxides as pinkrosa, ferric oxide, chromium oxide, cadmium sulphide, etc., which develop rose, red, green, and yellow colours respectively. In many cases a little zinc oxide (2 per cent.) is also added to make the white enamel more fiery.

Clay serves as a further important addition to the grinding process for every enamel, since it possesses to the highest degree, due to its finely divided condition, the capacity of holding the ground-enamel in a state of suspension, and thus preventing the so-called "settling." Moreover, the clay produces opacity and influences most favourably the elasticity of the enamel. The preliminary treatment of the clay has been already described. The addition of stannic oxide to white enamel varies from 5–18 per cent., that of clay from 5–13 per cent. Only 3–6 per cent. clay is added to ground and blue enamels.

It is also advisable to use in certain cases a so-called vehicle (*Stellmittel*) with the enamel, unless one prefers to do this immediately before charging the working-dishes with enamel.

The vehicles used are for the most part alkaline, seldom of an acid character, and serve to stiffen the enamel, so that, on taking a sample in a ladle, the enamel is only mobile for a few seconds and then quickly comes to rest. The enamel is then said to stand good.

The principal vehicles to be noticed are sal-ammoniac, ammonium carbonate, magnesium chloride, burnt magnesia (formed by heating magnesium carbonate to redness), common salt, and, for many enamels, borax and soda. Often Epsom salts and magnesium sulphate are used. Most worthy of recommendation for white enamels are ammonium carbonate and burnt magnesia. The former has the valuable property of volatilising in the muffle without leaving behind the often injurious chloride and sulphate. Burnt magnesia also commends itself as a pure base free from acids. For ground and blue enamels borax is readily used as a vehicle (about 50 60 grm. per 100 kg. enamel). With such powerful substances for vehicles a caution must be uttered. The enamel expert will always find for individual cases the correct minimum amount to add of these unavoidable vehicles, and from fundamental reasons this important post in an enamel works is never given to workmen. It has happened that workmen who appeared conversant with the use of such materials have often used highly objectionable salts as vehicles, and in consequence have been severely reprimanded.

Finely ground enamels have a brighter lustre than those more coarse; yet in spite of this the enamels are not powdered too finely, since they acquire a soapy, slimy feel and are hard to use, owing to the formation of lumps.

Ground and blue must be somewhat more coarse-grained than white. In cases where the utensil is only to be coated once with white enamel, it must be ground correspondingly coarser than a so-called second white, which is used for the second covering.

The specific gravity of the enamels, *i.e.* the weight of a cubic centimetre, amounts to:—

For white, calculated without included water	2·8
The same reckoned + 35 per cent water	1·8
For ground enamels, calculated without included water . . .	2·04
The same reckoned + 35 per cent. water	1·55

According to the ordinary formula, $v \times s = g$, *i.e.* the product of volume and specific gravity of a body is equal to its weight. The weight of a volume of the enamel, or *vice versa*, may quickly be calculated by using the above specific gravities.

E.g. a vessel contains 45 litres of white enamel powder, including water, and therefore ready for use. This 45 l. weighs, therefore, 45 × 1·8 = 81 kg.

The same vessel containing 45 l. ground-enamel will only weigh 70 kg., since 45 × 1·55 = 70 kg.

The specific gravity of white enamel is higher than that of the other enamels, owing to the addition of stannic oxide, and approaches, consistent with similarity in character, the specific gravity of glass, which varies from 2·4–3.

The cost of fusion for 100 kg. enamel, from the ratios of the amounts melted, will be determined by the sum of the following variables: crucibles for melting, fire-proof material, boxes for holding the enamel, coal for the furnace, shovels and similar implements, the wages of the smelters, bricklayers, locksmiths, and tinners.

The cost entailed in the grinding is in its turn similarly calculated from the amount of work done in a month, wages, repairs, and materials used. The calculation of the complete enamel, ground moist and ready for use, is reckoned, however, without water, and may be rapidly made on the basis of the following formula:—

Pr stands for the cost in shillings of 100 kg. of the mixed, unheated enamel.
Pz = value in shillings of the additions to the grinding.
I. = cost of fusing 100 kg. enamel
M = cost of grinding 100 kg. enamel.
Z = the percentage additions to the grinding
Pm = the cost of 100 kg. enamel ready for use, and including all the additions, with the exception of water.

$$Pm = \frac{(100\,Pr + Pz + I)\,100}{100 + Z} + M.$$

If for white enamel the additions average 16 per cent., then the formula approximately reads :—

$$Pm = Pr + 0·85 \times Pz + L + M.$$

In many works the powdered white enamel is subjected to a further purifying process. The success attained for the latter requires notice, but the process is not recommended for ordinary use, on account of the relatively high expense. To blue enamel a little ferric oxide is advantageously added on grinding, whereby the blue will be rendered more brilliant and intense.

The enamel fragments produced during the operation should as far as possible be separated according to colour, collected together, and fused, for further addition in suitable quantity to the blue enamel before melting, *e.g.* :—

BLUE ENAMEL.

Borax	60·0 kg.
Alumina	3·6 ,,
Felspar	101·5 ,,
Soda	6·2 ,,
Natural cryolite . . .	24·0 ,,
Saltpetre . . .	2·5 ,,
Fused enamel, fragmentary .	40·0 ,,
Cobalt oxide . . .	3·0 ,,
Limonite	0·3 ,,
Ferric oxide . .	0·1 ,,
	241·2 kg.

Additions on grinding:

$4\frac{1}{2}$ per cent. purified levigated clay.

120 grm. ammonium carbonate per 100 kg. enamel.

The following further formulæ, etc., may be given for some special varieties:—

BLACK FUSED ENAMEL.

Borax	62 kg.
Felspar	120 „
Soda	14 „
Ferric oxide	8 „
Cobalt oxide	2 „
Smalt	16 „
Limonite	16 „
Total	238 kg.

ACID RESISTING WHITE.

Borax	74 kg.
Felspar	100 „
Quartz	115 „
Cryolite	47 „
Stannic oxide	40 „
Fluorspar	[illegible] „
Soda	20 „
Saltpetre	10 „
Magnesium carbonate	1 „
Pure powdered glass-meal	50 „
Clay	12 „
Calcspar	6 „
Total	484 kg.

Additions on grinding :

7 per cent. clay.
6 ,, tin oxide.
$\frac{1}{3}$,, burnt magnesia.

GLAZE.

Borax	21 kg.
Quartz	60 ,,
Felspar	40 ,,
Cryolite	12 ,,
Saltpetre	4 ,,
Soda	8 ,,
Fluorspar	6 ,,
Total . .	151 kg.

WHITE, FOR CORAL RED, ETC.

Borax	60 kg.
Felspar . . .	58 ,,
Quartz	34 ,,
Soda . . .	6 ,,
Cryolite	11 ,,
Clay	4 ,,
Total . .	173 kg.

Additions on grinding :

4 per cent. clay.
7-10 per cent. coral red substances.

Among the enamels suitable for hardware, the following may be mentioned:—For ground-enamels a matted ground is used, *i.e.* a substance which has only been heated in the furnace to the melting point, and which on account of its composition is excluded from complete fusion. This matt is prepared by mixing together borax, quartz or flint, felspar, fluorspar, and clay. Naturally, a number of formulæ exist, from which the following are selected :—

		Additions on grinding.
(1)	30 kg. quartz.	$8\frac{2}{3}$ kg. clay.
	17 „ borax.	$\frac{1}{2}$ „ magnesia.
(2)	30 kg. quartz.	$10\frac{3}{4}$ kg. clay.
	30 „ felspar.	6 „ felspar.
	25 „ borax.	$1\frac{3}{4}$ „ magnesia.

(3) 210 kg. flint, 70 kg. borax, 10 kg. soda are fused for three to four hours in the furnace. During grinding, 32 kg. of the melt, 11 kg. clay, 34 kg. quartz are added.

		Additions on grinding.
(4)	28 kg. flint (silica).	18 kg. of the melt.
	8 „ borax.	6 „ quartz.
	1 „ fluorspar.	1·5 „ clay.

This mass is known as the matt (*Fritte*), and is prepared by mixing the substances named, and heating to redness in a shallow pan, covered externally by clay, in the muffle furnace. The heating lasts about one to one and a half hours.

The matt forms a porous, tuff-looking mass, which is broken up and ground moist in the mill with the addition of the other substances. A too abrupt fusion of the matt is avoided, otherwise a loss of adhering power is entailed.

All the good white enamels for sheet metal may be used for enamelling hardware. Many cast objects, such as imitation majolica, baths, etc., should not be covered by enamels ground moist, but with those powdered by hand or by means of a sieve or special machine. The process of covering a cast object which is red hot with dry enamel finely powdered will be understood a little later. The enamel used must be easily fusible, and the process is performed with repeated warming of the object, until the enamel layer has the desired thickness. Vessels so treated present a porcelain like appearance, but are expensive. Frequently the ground white enamel may be sprinkled direct on the red glowing cast without the intermediate stage of a matted ground.

Many enamel powders are prepared with lead, antimony, or arsenic compounds, which give an extraordinary lustre to the enamels.

An enamel containing arsenic is easy to recognise, since in fused samples it exhibits a bluish, gleaming, translucent edge.

As an example of a white enamel powder free from poison may be taken :—

Borax	[illegible]	kg.
Felspar	[illegible]	,,
Stannic oxide	60	,,
Clay	20	,,
Soda	8	,,
Saltpetre	2	,,
Natural cryolite	40	,,

Ammonium carbonate . .	3 kg.
Fluorspar	2 ,,
Magnesium carbonate . .	2 ,,
Total	465 kg.

As a further example of a white enamel for covering cast iron when moist :—

Borax	62·0 kg
Felspar	60·0 ,,
Soda	4·0 ,,
Cryolite	20·0 ,,
Saltpetre	3·0 ,,
Clay	2·5 ,,
Stannic oxide . . .	2·0-5·0 ,,
Magnesia	0·2 ,,
Fluorspar	0·1 ,,
Total	153·8 kg.

Additions on grinding:

7 per cent. tin oxide,
7 ,, clay, and
0·3 ,, magnesia.

[TABLE.

THE CHEMICAL COMPOSITION OF SEVERAL ENAMELS

Number.	Species of Enamel.	Silica (SiO_2).	Alumina (Al_2O_3).	Lime (CaO).	Magnesia (MgO).	Sodium Borate ($Na_2B_4O_7$).	Sodium Oxide (Na_2O).	Potassium Oxide (K_2O).	Stannic Oxide (SnO_2).	Antimony Oxide (Sb_2O_3).	Phosphoric Acid (P_2O_5).	Cobalt Oxide (Co_2O_3).	Ferric Oxide (Fe_2O_3).	Boric Acid (B_2O_3).	Limonite.
1	White, easily fusible	39·38	10·3[illegible]	0·75	...	21·[illegible]3	7·[illegible]	8·[illegible]1	11·[illegible]0		...	...	...	...	...
2	White, easily fusible	44·[illegible]	0·5[illegible]	0·[illegible]		21·[illegible]	11·[illegible]	1·[illegible]9	11·4[illegible]				...		...
3	White, easily fusible	[illegible]4·23	5·07	[illegible]·63	3·4[illegible]	25·7	9·73	1[illegible]·0[illegible]	[illegible]·3	.	.	...	...		...
4	White, hardly fusible	47·28	2·2	[illegible]·[illegible]3	4·8[illegible]	[illegible]8·70	2·[illegible]8	8·9[illegible]	9·5				...		...
5	White, easily fusible	3[illegible]·72	1[illegible]·0	2·9[illegible]	5·7[illegible]	2·[illegible]5[illegible]	[illegible]·95	11·23	12·2[illegible]	.			...	...	...
6	White, stable to a[illegible]	[illegible]·[illegible]0	5·5[illegible]	5·58	[illegible]·26	.	12·[illegible]5	2·[illegible]4	2·0[illegible]	...	[illegible]·3[illegible]	.	...	9·83	...
7	White	41·48	11·[illegible]7	4·1[illegible]	[illegible]·05		11·9[illegible]	2·14	17·38		[illegible]·11		...	8·62	...
8	White	35·[illegible]	15·0	3·5[illegible]	[illegible]·22		[illegible]	3·3		[illegible]·80	.	.	...	17·32	...
9	White	41·50	1[illegible]·7[illegible]	0·93	[illegible]·47	...	13·2[illegible]	5·73	14·28		0·15	[illegible]·08	...	10·70	...
10	Blue	53·16	15·89	0·55	0·22	...	13·[illegible]2	5·83	0·34	...	0·17	1·26	2·23	5·60	0·25

EXAMPLES OF MIXTURES CORRESPONDING TO THE ABOVE ANALYSES.

No. 1 is the analysis of an easily fusible white body-enamel, the mixture being made up of :—

Felspar	60	kg.
Borax	42	„
Tin oxide	12	„
Soda	15	„
Saltpetre	2	„

No. 2 is the analysis of a white enamel consisting of :—

Felspar	27·0	kg.
Borax	35·0	„
Quartz	20·0	„
Tin oxide	17·0	„
Soda	16·0	„
Saltpetre	2·5	„

No. 8 is white enamel mixed from :—

Borax	47·0	kg.
Felspar	46·0	„
Antimony oxide	9·2	„
Soda	1·4	„
Clay	4·5	„
Cryolite	16·2	„

CHAPTER IV.

THE PREPARATION OF THE CRUDE WARE.

THE crude wares are heated to redness before pickling, with the object of removing the adhering, greasy or soapy layer. Moreover, the elasticity of the sheet metal, which is lost during the forging, drawing, planing, or pressing processes, is restored by heating, this operation being conducted for the most part in the muffle, seldom in a special furnace. If the crude wares are dipped in weakly acidified water before heating, the process is rendered more thorough since the oxide or scale layer easily comes off after glowing. With better-class wares this should always be done. Many of the flaws which show themselves in the enamelled utensil after firing have their origin in the incomplete and therefore insufficient heating of the crude wares.

Above all, too many wares should not be heated at the same time. Washing utensils, plates, etc., are placed in sets of not more than five to eight pieces. If, for example, washing utensils in piles containing twenty or more pieces are heated, then incomplete combustion of the impurities takes place, together with a non-uniform oxidation in consequence of the scarcity of oxygen. The latter often causes afterwards a chipping off of the enamel at the edges of the utensil. Bad heating is generally an accompanying cause of scale formation (nail-chips, *coup d'ongle*), so that, on cooling, small enamel particles in the form of a miniature finger-nail break off from the fired enamelled ware. It should not be supposed that this, which is so feared by the workman, can only be traced to improper heating, since scale formation is often due to insufficient burning in of the ground enamel, or to a faulty enamel. In order, however, to avoid a usual error during manufacture, which may be ascribed to different and often not permanent causes, the careful man will use all the means which experience has placed at his disposal.

It is folly to pack together for heating cylindrical or conical objects, such as pots, stewpans, etc., for the grease will only be incompletely burnt, and carbon deposited, which will be drawn into the pores of the metal. When enamelling such objects, a more or less thick blister formation takes place on the sides and edges, causing an increased percentage of damaged goods.

The temperature of the furnace must be suitable (about 750° C.) and kept uniform. An underheated furnace, in which the crude wares must remain over long, is as injurious as one overheated.

As in the preliminary treatment of hardware, so in other cases, it is advisable to heat gently in the muffle before pickling, in order to burn up the adhering coal-dust.

The crude ware so prepared is now taken to the pickling chamber. The pickling has for its object the production of a pure metallic surface, since only upon such will the ground-enamel adhere, and on burning unite with it.

At the same time, during the pickling, the metallic surface will become rough, causing the enamel to adhere better and more intimately. As pickling, liquid hydrochloric acid is generally used, seldom sulphuric. The latter is employed more especially for cleansing cast wares, although many firms pickle with hydrofluoric acid, which dissolves at the same time the adherent or more deeply embedded sand particles derived from the sand mould or blast.

How deep the sand particles may penetrate into sheet metal when exposed to the sand blast, follows from the remarkable fact that such metal, when as pure as it is possible to obtain it and in spite of an additional immersion in acid, is no longer capable of being tinned. The tin will only alloy itself at isolated spots on the metal.

Dilute hydrochloric acid is used, one-third acid of 21 Bé (specific gravity 1·171) to two thirds water. The sulphuric acid for pickling is prepared from

90 parts water and 10 parts concentrated acid of 64° to 65° Bé (specific gravity 1·795–1·820). For cast iron, since hydrofluoric acid is not used, dilute sulphuric is taken, and heated by means of steam. Hydrochloric is preferable to sulphuric acid, being not only cheaper, but also causing less inconvenience in breathing. The acid must be free from arsenic, otherwise arseniuretted hydrogen will be evolved during the pickling, and this possesses a disagreeable garlic-like odour, and is, moreover, injurious to health.

It is advantageous to test the pickling agent daily for the amount of unused acid. A test quantity is titrated with semi-normal caustic soda solution to which a little sugar has been added to avoid oxidation of the dissolved ferrous salt. Phenolphthalein is used as indicator during the analysis. This test may be carried out in a few minutes by any intelligent workman.

If the frequent control of the acid liquor be neglected, it may happen that either too little or too much fresh acid will be added daily.

Sorel[*] recommends the following for cast iron:—

96 parts sulphuric acid of 10° Bé.
4 „ tin salt ($SnCl_2$), or zinc chloride ($ZnCl_2$).

If the acid content be too small, the amount of ferrous salt in the acid baths will be too great, and inadequate duty done; besides, the cleansed crude ware will be tarnished by a yellow coating of ferric oxide.

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[*] Dingl. Polyt. Journal, cvii. 400.

If acid be added too frequently and in too great quantity, then the process will be too energetic. Iron will be dissolved unnecessarily at the expense of the excess of acid, and this quite apart from the material disadvantage due to acid waste.

A mud gradually settles on the floor of the acid vessel or vat, arising from the undissolved tin, separated ferric oxide, etc. The vat must therefore be cleaned out from time to time, and this is done by scooping out the mother liquor into a wooden vat (old casks) and allowing the mud to settle. The clear upper liquid is replaced in the pickling vat, and the required amount of fresh water and pure acid added.

A pickling solution prepared without the addition of old mordant liquor acts very slowly at first, a fact which may be traced to the catalytic influence of hydrogen gas dissolved in the acid. If at first the cleaning liquor has absorbed a relatively large amount of hydrogen, its activity will be brisk, and therefore the addition of the old mother liquor, which is rich in hydrogen, is necessary, as well as economical. The greater part of the pickling liquor is lost in adhering to the wares and to the particles torn from the acid bath.

To what degree loss of metal is caused by pickling is shown by the following example of a roll 20 cm. in diameter and of varying thickness :—

THE LOSS OF METAL DURING PICKLING.

Diameter of the Roll, in mm	Thickness of the Metal in mm.	Surface, in sq. cm.	Net Weight, in gr.		Loss due to Pickling (metallic loss).
			Before Heating and Cleansing.	After Cleansing.	Per cent
20	0·25	628	55	52·25	5·0
,,	0·30	,,	66	63·25	4·10
,,	0·35	,,	77	74·25	3·50
,,	0·40	,,	88	85·25	3·10
,,	0·45	,,	99	96·25	2·80
,,	0·50	,,	110	107·25	2·50
,,	0·55	,,	121	118·25	2·30
,,	0·60	,,	132	129·25	2·10
	0·65	,,	143	140·25	1·90
	0·70	,,	154	151·25	1·80
	0·75	,,	165	162·25	1·70
	0·80	,,	176	173·25	1·50
,,	0·85	,,	187	184·25	1·40
,,	0·90	,,	198	195·25	1·38
	0·95	,,	209	206·25	1·31
,,	1·00	,,	220	217·25	1·25

The crude wares suffer a loss in weight on pickling which averages 2–4 per cent. The problem as to which is the best material for making the most serviceable pickling vats is hard to solve. Tanks made of granite or earthenware are very durable, but too expensive and, moreover, limited in capacity. Also vessels prepared from slabs of glazed stone are unsatisfactory. The most suitable are those thoroughly coated inside with lead, which in its turn is covered by wood. Between the wood and lead Goudronteer or Frankfort asphalt is poured. A limpid pickling agent acts more quickly and saves any subsequent rubbing or scrubbing of the cleaned ware.

The metallic object to be pickled is placed in a latticed basket and set in the acid bath. The process lasts from 30–45 minutes, according to the concentration of the bath and the thickness of the metal. For the ware to remain too long in the acid is injurious, on account of partial decomposition of the material and the formation of so-called metallic blisters. The sheet metal is composed of many layers, and the pressure of the hydrogen evolved produces an inflation, *i.e.* a blister. A rusted crude article which has suffered much atmospheric exposure requires prolonged pickling, and becomes of inferior quality because of rust formation and the unequal action of the acid. The pickled ware is placed in a water tank in order that the greater part of the acid may be removed. The last traces of acid adhering are neutralised by dipping the objects in boiling soda, frequently merely milk of lime solution. The cleansed ware is then rapidly dried on a special drying hearth. This drying must follow as quickly as possible, to prevent fresh oxidation. Hollow handles, etc., require a specially careful and thorough drying.

Pickling hardware likewise requires much care. The ware remains in the hot 10 per cent. sulphuric acid about 1 to 1½ hours, is then placed in pure water, and finally in boiling soda solution. After it has been so treated, the cast is cleaned or scrubbed once more by wire brushes, using a large amount of water.

The faultless preparation and removal of the acid liquor often involves expensive and difficult work. In several countries the legal regulations respecting this are very lax, but in Germany a conscientious observance of very stringent laws is strictly enforced.

Where sufficient running water is at hand, with which the waste acid liquors can mix in a minimum ratio of 1 : 10, the liquor-removal problem has a simple solution. In other localities the contrary is the case. By neutralising the acid liquor with milk of lime and soda, leading the same into oxidation reservoirs where the ferric oxide for the most part separates out and settles, filtering the neutral liquor through powerful filter presses in order to retain the last particles of mud, and then allowing this liquor to filter through land in percolating ponds, it is possible to remove in reality all danger of contaminating running water.

Some German enamel firms have set up complete plants for the thorough neutralisation and separation of mud from their acid liquors.

How far the purification of acid water may be accomplished in the manner described is shown by the following illustrations :—In a large German ironworks the impure acid waste liquor shows the follow- average composition :—

100 litres contain :

Sulphuric acid	70·08 grm.
Iron	43·96 „
Chlorine	0·62 „

After purification by neutralisation, filtration, etc., this waste liquor is made up as follows :—

100 litres water contain :

Solid constituents	6·920	grm.
(*a*) inorganic	5·080	,,
(*b*) organic	1·840	,,
Chlorine (Cl)	0·592	,,
Sulphuric acid (SO_3) . . .	0·820	,,
Lime (CaO)	1·600	,,
Magnesia (MgO)	0·362	,,
Iron (Fe)	0·018	,,

The organic substance present in 100 litres, expressed in terms of potassium permanganate ($KMnO_4$) = 1·94.

At all events the chemical purification of waste acid liquor has been carried out on a large scale with marked success.

CHAPTER V.

THE PROCESS OF ENAMELLING.

The cleaned crude ware is further examined for accidental bruises, these being removed by beating out with a wooden hammer, a process now conducted in the principal workroom of the enamel works.

The coating of the cleaned utensil with enamel is done in accordance with definite rules and manipulations, and is known as the "laying" of the enamel. The workmen entrusted with the operation are called "enamellers."

The art of covering can only be acquired by long practice, and requires intelligent, educated workmen, since every kind of utensil, however different its shape, must be provided with the enamel coating by a suitable rolling movement.

There are distinguished the so-called "primary coating," the first white, the second white or protecting coat, and the coloured enamel coatings. An immediate covering or enamelling of the cleaned crude ware with white enamel is impossible, for the latter, by virtue of its composition, possesses an expansion coefficient essentially different from that of iron. Moreover, the stannic oxide content of the white enamel brings about a blister development, since this oxide is reduced by the carbon present in the iron at the heat of the muffle. Before the white coating the crude ware must therefore be provided with an enamel cover possessing very definite chemical and physical properties. The enamel used is known as ground-enamel (*Grundemaille*), and is essentially an easily fusible substance, coloured by cobalt or nickel oxide with a little limonite. The requisite amounts of these oxides, in union with borax, give to the ground-enamel a coefficient of expansion approaching quite near to that of sheet iron. The same composition minus cobalt or nickel oxide would be useless.

The search for a ground-enamel free from cobalt and nickel oxide still remains a problem for the expert, and it may be safely asserted that the previous formulæ for such white primary enamels must be regarded as humbug.

In recent years partial success has been realised by replacing the expensive cobalt oxide in the ground-enamel with the much cheaper nickel oxide, but this requires careful attention, and the enamel so prepared is inferior to the cobalt oxide primary in stability and elasticity. For high class wares a ground-enamel coloured by cobalt oxide is therefore employed.

The ground enamel should be fairly dilute (40 per cent. water) and coarse-grained, and the primary coating should be as thin as possible. A small plate of sheet metal coated with ground-enamel should, after the burning in of the enamel, be capable of being bent without the ground-enamel chipping off at the edge of the bend.

The average output of a man working with the ground-enamel lies between 200–300 pieces (150–300 kg.) for large, and from 300–1500 pieces (200–400 kg.) for small utensils, in the course of a ten-hour day. Naturally, such numbers are subject to great fluctuation, when the many varieties and sizes of utensils are taken into account.

The vessels covered with ground-enamel must be rapidly dried, and for this purpose specially constructed stands are used, which are heated by steam-pipes, or more generally by the hot gases from the muffle furnace. Should rapid drying be omitted, then rust easily develops, and the damp wares then exhibit rusty-brown stains. A moderate addition of borax frequently prevents this partial rust formation. In the case of ground-enamels used for cast iron or for matts the same treatment serves, yet in this case only borax which has been previously fused and dissolved in hot water is added.

Care must be taken that wares coated with primary enamel show no damaged metallic places after drying, since in the subsequent firing these places are changed to ferrous oxide and so give rise to faulty goods. An article carefully covered with primary enamel and then fired forms the basis for future treatment. A covering ground-enamel prepared too concentrated is equally as bad as one too dilute. It is the business of the enamel master to be convinced repeatedly during the day of the consistence of the ground-enamel, for, should this be too fusible relative to the next coating, then a blister development in starry form will be found on the finished product.

The introduction of ground enamels prepared from new formulæ should be cautiously made, since nothing can endanger the trade or inflict greater injury on the owner than a careless, hasty importation of a new ground-enamel.

The weight of ground-enamel necessary for 1 kg. crude ware, supposed to be of average metallic thickness, varies from 80-100 grm., *i.e.* 8-10 per cent. The firing of well dried ground-enamelled sheet ware is conducted in the muffle furnace at a temperature of 950-1000° C., corresponding to the varying composition of the ground enamels in the different works. The utensils, on being coated with ground-enamel, are submitted to a more severe burning in than that given for the next covering. The borax, which is present in ample proportions in the ground-enamel, requires a fairly large amount of heat to become a mobile liquid, and so unite intimately with the metal.

After the firing of the wares coated with ground enamel, the next operation is the enamelling with white enamel. In the case of many inexpensive wares only one white coating is put on, but the majority require a second. At this stage mention might be made of the circumstance that the great expectations entertained by the introduction of methods having for their object a single white coating have only been partly realised.

Every expert who, without wishing to deceive himself and others, would follow his convictions, must confess the unsuitability of the so-called single white coatings for special qualities of ware. The single white coating, since it must be laid on thicker to be sufficiently white, causes an average of 20–30 per cent. in repairs or patchwork. Moreover, the cover will have his working capacity limited, and in reality will produce less than if two white coatings were put on. The patched wares generally require a further firing and another coating, so that such utensils are often unfavourably distinguished from other wares by their multitude of coats.

On the other hand, it is certain that for export, where often the tax is reckoned according to the weight and low price attached to wares which have only been white enamelled once, then what is lost in beauty is gained in the solidity consequent on a thinner enamel layer, since the thickness of the covering has a great influence on the durability of the ware, for the quality is inversely proportional to the thickness of the enamel layer, and directly to the cross section of the sheet metal.

For enamelled hardware the following data of enamel consumption hold good :—

The ground coating amounts to	0·90 per cent.,
The inner coating of white enamel to	4·20 „
The outer asphalt painting to .	0·24 „
And the loss on etching to .	0·30 „

of the final weight.

THE INCREASED WEIGHT OF METALLIC OBJECTS AFTER THEIR PRIMARY COATING.

A Roll (Tube) of Diameter, in cm.	Thickness of the Sheet Metal, in mm.	Surface, in sq. cm.	Net Weight, after [illegible], in grm.	Weight of the Roll after being Coated by the Ground Enamel, in grm.	Consumption of Ground Enamel,	
					in grm.	per cent.
20	0·25	628	52·25	62·35	10·1	18·3
„	0·30	„	63·25	73·35	„	15·3
„	0·35	„	74·25	84·35	„	13·1
„	0·40	„	85·25	95·35	„	11·5
„	0·45	„	96·25	106·35	„	10·2
„	0·50	„	107·25	117·35	„	9·2
„	0·55	„	118·25	128·35	„	8·3
„	0·60	„	129·25	139·35	„	7·6
„	0·65	„	140·25	150·35	„	7·1
„	0·70	„	151·35	161·35	„	6·5
„	0·75	„	162·25	172·25	„	6·1
„	0·80	„	173·25	183·35	„	5·7
„	0·85	„	184·25	194·35	„	5·4
„	0·90	„	195·25	205·35	„	5·1
„	0·95	„	206·25	216·35	„	4·8
„	1·00	„	217·25	227·35	„	4·6

Objects which are to receive a second coating of white enamel should be as thinly enamelled as possible the first time. The second coat should give strength and appearance to the ware, and must be laid on with the greatest care.

Enamelled objects are usually provided with a red enamelled border, which is prepared either after the first or, in some cases, only after the second coating.

A neat border gives a pleasing harmonious appearance to the ware, and therefore too much care cannot be exercised in its preparation.

Whether the so-called border or "anrollen" is made by hand or by rolling the utensil on a plane steel slab, depends on the respective works' routine. The bordering by means of a steel plate is made in a thin layer on the blue or black enamel, and gives a faultless edge.

The drying of the utensil enamelled in white or blue has usually to take place slowly, without the aid of a special source of heat, *i.e.* in the air. On the other hand, the white enamelled cast wares may be safely dried on a moderately heated hearth, and during the process every kind of vibration must be avoided.

It may be usually accepted that enamelled sheet wares are stable against rapid temperature change. Thanks to the present position of enamel technique, the preparation of a really durable ware is thoroughly understood. Where, however, a small capacity of resistance against abrupt temperature change is found, this may be traced to a variety of causes. The cover enamel must, under all circumstances, be suitable for the ground, just as the crude ware must be carefully prepared, in order to obtain the correct tension, especially at the base of the utensil. The basal curve of a forged utensil should be as round as possible, since the tension differences are expressed usually at the centre of the base. With respect to this, a new process of a well-known enamel firm deserves mention, who attain an increased stability of the base by pressing in the centre diagrams standing in relief, such as trade-marks or similar impressions. The diameter of this relief should usually amount to one-seventh of the base. This idea is at all events worthy of note.

The total amount of enamel required by the finished enamelled sheet ware depends naturally on its size, and is usually expressed as a percentage of the final weight.

The following table shows the varying percentage enamel content of utensils of varying thickness :—

THE CONSUMPTION OF ENAMEL.

Thickness of Sheet, in mm	Percentage Enamel Consumption.	
	Calculated upon the Initial Net Weight.	Calculation from the Final Weight.
0·10	128·0	56·0
0·20	64·0	39·0
0·25	43·0	30·0
0·35	37·0	27·0
0·40	32·0	24·0
0·50	26·0	20·0
0·60	21·0	17·6
0·70	18·0	15·5
0·8	16·0	14·0
0·9	14·3	12·5
1·00	12·5	11·0
2·00	6·4	6·0
3·0	4·3	4·0

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* Kl. 48c. Process for preventing the chipping away of the enamel on account of the inequal tension developed by the action of heat. D.R.P. angem. St. 10,256. Stanz- und Emaillirwerk vorm. Carl Thiel & Söhne, A. G., Lubeck.

INITIAL WEIGHT OF METAL.

Thickness of Sheet, in mm.	1 Sq. Metre of Sheet weighs kg.	Thickness of Sheet, in mm.	1 Sq Metre of Sheet weighs kg.
0·10	0·78	0·70	5·46
0·20	1·56	0·80	6·24
0·30	2·34	0·90	7·02
0·35	2·73	1·00	7·80
0·40	3·12	2·00	15·60
0·50	3·90	3·00	23·40
0·60	4·68		

Since most of the saleable utensils are prepared from sheet metal of 0·3–0·5 mm., the usual quantity of enamel required, amounting to 25–30 per cent., is calculated on the final weight of the object. In practice the true enamel consumption is really greater, in consequence of the unavoidable loss during the transit of the powdered enamel to the coating saucer, but chiefly during the covering operation itself. The object in all firms is to reduce to a minimum this over-consumption of enamel. The wash-waters from the separate coating saucers, as well as other enamel residues, are collected and carefully separated according to colour, in order that some may be directly used again after careful sieving for the first white covering, or remelted in the furnace and added to the colour enamel mixture. Only by noting exactly the enamel entry, and comparing this with the monthly production of enamelled wares, will one be able to determine the true amount of enamel consumption, and be in a position eventually to put a stop to waste.

CHAPTER VI.

FIRING THE ENAMELLED WARES.

THE so-called burning in or firing of the enamelled wares is conducted in the muffle, and has for its object the fusion of the enamel coating.

It has been mentioned that the burning in of the ground-enamel takes place at a high temperature (950–1000° C.) and requires an average time of 3-4½ minutes. The white coating and also the blue require a somewhat lower temperature (about 800–850° C.) and a duration of 3½-4 minutes.

By an insufficient furnace temperature, or duration of burning in, the ware deteriorates in lustre.

At too high a temperature the white enamel will become glassy, lose its opacity, and appear common. The property of stannic oxide in producing opacity depends on the fact that, at a temperature up to 900°, it remains finely suspended in the molten enamel without dissolving, but at a higher temperature partial solution takes place, with the formation of tin silicate, which causes the white enamel to lose its covering power.

The modern furnaces have a muffle length of 1·80–2·50 m., a breadth of 80–110 cm., and a height of 70–95 cm. The muffles are composed of several shaped pieces or form single plates, but the latter are less worthy of recommendation. Double muffles, viz. two muffles heated by the same firing, are generally disadvantageous, since in case of repairs the first as well as the second muffle must be thrown out of action.

According to the mode of firing, the furnaces are distinguished as direct, semi-gas, or regenerative. With the increasing price of coal, direct firing is absolutely unprofitable, since a greater part of the heat is drawn away unused into the conduits. Semi-gas firing with stepped, plain, or fissured grates is most trustworthy, especially in works of average size where the heat is drawn away for use at the drying hearths.

Regenerative firing is, however, without a doubt the best, because it is technically the most complete. The fuel in the generators is transformed by incomplete distillation into carbon monoxide, and this combustible gas is burnt immediately to carbon dioxide in the conduits of the muffle by union with the previously heated air.

For the rational carrying out of the firing, the repeated analysis of the gases at the places where generated, viz. in the generator as well as immediately in front of the place of combustion (and therefore before union with the combustible air), is absolutely necessary. This analysis, together with the examination of the conduit gases after combustion, affords the most certain guarantee for proper working, since it prevents the waste of coal and exposes defects.

It is important to know the content of carbon dioxide and carbon monoxide in the gas. Carbon monoxide varies from 20-30 per cent., while good generator gas should not contain more than [illegible] per cent. carbon dioxide. Through many generators steam is conducted for the purpose of obtaining an increase of temperature due to the partial formation of water gas.

In this case the gas should contain :—

Hydrogen . . .	up to 27 per cent.
Carbon monoxide . .	[illegible] ,,
,, dioxide . .	[illegible] ,,
Methane	1 ,,

The heavier hydrocarbons are seldom present in generator gas.

The gases given off, i.e. the gas after combustion, should contain [illegible] per cent. carbon dioxide and [illegible] per cent. oxygen.

The average temperature of the gas produced varies from [illegible] C.

The gas analysis is most appropriately carried out with an Orsat or Orsat Schwackhöfer portable apparatus. The apparatus possesses three absorption vessels, the first being full of caustic potash solution (sp. gr. 1·[illegible]) for the absorption and determination of the carbon dioxide content, the second is filled with mixture of pyrogallic acid (18 gr. in 40 c.cm. hot water) and caustic potash (sp. gr. = 1·28) to absorb the oxygen in the generator gas; and the last absorption vessel contains a cuprous chloride solution (35 gr. cuprous chloride + 200 gr. hydrochloric acid and 50 gr. of sheet copper turnings) to absorb the carbon monoxide. The manipulation of the apparatus is simple, and the analysis performed in a few minutes.

Gas analysis should generally find an extensive application in our industry, and up to the present this has been the case. The saving in coal realised by a well-regulated production of generator gas is very important.

At this stage a few words must be said concerning another measuring instrument, the use of which, for controlling the furnace temperatures necessary in a modern factory, is indispensable. This is the pyrometer or thermometer.

Distinction must be made between the water pyrometer, clay pyrometer or "segerkegel," electrical and optical pyrometers.

The segerkegel (clay pyrometer) consists of a small baked clay cone, which, corresponding to its varying content of alumina and silica, melts at different temperatures. In the enamel industry, where the temperatures employed vary from 800-900° C., clay pyrometers from Nos. 015 to 06 are chiefly used.

The connection between the number, chemical composition, and temperature is given by the following table :—

Clay Pyrometer No.	Chemical Composition			Temperature of Fusion.
				C.
015	0·5 Na_2O 0·5 PbO	0·6 Al_2O_3	3·2 SiO_2 1 B_2O_3	800
014	0·5 Na_2O 0·5 PbO	0·65 Al_2O_3	3·3 SiO_2 1 B_2O_3	830°
013	0·5 Na_2O 0·5 PbO	0·7 Al_2O_3	3·4 SiO_2 1 B_2O_3	860°
012	0·5 Na_2O 0·5 PbO	0·75 Al_2O_3	3·5 SiO_2 1 B_2O_3	890°
011	0·5 Na_2O 0·5 PbO	0·8 Al_2O_3	3·6 SiO_2 1 B_2O_3	920°
010	0·3 K_2O 0·7 CaO	0·2 Fe_2O_3 0·3 Al_2O_3	3·5 SiO_2 0·50 B_2O_3	950°
09	0·3 K_2O 0·7 CaO	0·2 Fe_2O_3 0·3 Al_2O_3	3·55 SiO_2 0·45 B_2O_3	970°
08	0·3 K_2O 0·7 CaO	0·2 Fe_2O_3 0·3 Al_2O_3	3·60 SiO_2 0·40 B_2O_3	990°
07	0·3 K_2O 0·7 CaO	0·2 Fe_2O_3 0·3 Al_2O_3	3·65 SiO_2 0·35 B_2O_3	1010°
06	0·3 K_2O 0·7 CaO	0·2 Fe_2O_3 0·3 Al_2O_3	3·70 SiO_2 0·30 B_2O_3	1030°

The use of the clay pyrometer requires time and is, moreover, expensive. In a special clay vessel a series of clay pyrometers are placed, somewhere in between the fusion points of the extremes of which the temperature is believed to be, and the particular cone which melts after half an hour is noted. From the number of the cone the temperature present is obtained.

Siemens and Halske's electrical pyrometer, "Le Chatelier," is more agreeable to manipulate.

The most convenient of all, and the one from which the temperature may most quickly be obtained, is the optical pyrometer (*lunette pyrométrique*) constructed by Von Ducretel in Paris. The principle involved is the property of a shining body (*e.g.* the red glowing muffle) to give a sensitive colour which may be denoted by a certain angle of rotation. This angle varies according to the composition, *i.e.* colour of the light, and therefore according to the temperature. The angle of rotation corresponds to the angle of the incident light of a glowing body upon the plane of polarisation of a quartz disc. This apparatus, in the form of a small telescope, renders ready and satisfactory service, the muffle temperature being read almost exactly in a few seconds. The point of the apparatus is set at zero, and it is turned while observing the glowing muffle until the appearance of the rose tint.

After this slight theoretical deviation we turn again to the firing of the enamelled sheet ware, when the following might be mentioned:—

It will always be assumed that the position of the fuel chambers is under and about the muffle, and that the combustion or union of the gases with air takes place as far as possible at the fore end of the furnace. Where this is not the case, we shall see that the rear of the muffle will be overheated, and the front part underheated. Therefore the rear set of wares to be fired will be finished instantly, while in front the objects placed there will not be fired sufficiently. Such an arrangement will naturally not suffice, and there will be inconvenience in consequence.

Odd wares suffer a deformation on firing, which must be set right again by treatment with a suitable shape. The operation is known as "Stösseln" (pestling), and must be performed immediately after firing, since the enamel has still a fiery glow and will therefore yield. As substratum for the form of the hot deformed objects a perfectly smooth horizontal iron slab serves, upon which an asbestos plate or a woven asbestos cloth is spread. A supplementary shape of the fired enamel cast ware is naturally impossible to obtain, as well as unnecessary.

The enamelled cast requires from 12–15 minutes for the proper burning in of the white enamel.

The outer black, tarry appearance remains so long as the ware is underheated.

The assortment of the wares to be fired should always take place immediately in front of the separate furnaces.

In every well-conducted works which depends principally on hand labour the unavoidable waste should not exceed 6–7 per cent.

A too strict supervision in order to reduce the unavoidable waste still further is unpractical, since the expense attached to it stands in no relation to the gain required.

The problem dealing with rational methods for reclaiming the crude ware from waste enamelled goods can scarcely at the present time be said to have been solved. The enamel is removed from larger and more valuable pieces, especially cast wares such as baths, by means of the sand blast. The removal of the enamel chemically with fused caustic alkalies has not up to the present proved satisfactory. More important progress in this direction appears to have been achieved by a new patent by Gustav Spitz of Brünn.*

The objects from which the enamel is to be removed are collected into a closed boiler and heated at a definite temperature under pressure with an alkaline or acid solution of fixed concentration.

The object from which enamel has been removed may be re-enamelled. The expensive enamel constituents may be reclaimed from the solution by well-known chemical processes for regeneration of the water solution.

This process actually gives good results with many firms, works economically, and appears to have succeeded in solving the question of removing the enamel satisfactorily from the waste goods by economical means.

A Few Remarks on Mistakes in Manufacture and their Possible Causes.—No branch of manufacture is dependent on such a number of factors for success as the ceramic industry generally, and the enamel industry in particular. With the best of intentions and the greatest indefatigability and experience, novel questions, fresh phenomena, and new problems are continuously presenting themselves to the expert.

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* D. R. P. No. 176,300, Kl. 48*d*. Gr. 5, and foreign patent: "Process for the removal of enamel from enamelled objects."

From the evidence afforded by the most complex errors, their cause cannot be fixed with certainty. The industry is unfortunately always dependent on too many conditions, viz. the quality of the sheet metal, the raw materials, the water, the construction of the furnace and temperature, on the heating, pickling, and enamelling, and finally on the composition of the enamel.

It is sought, below, to bring in a tabular form the most important failures in connection with their possible causes, but the author is well aware of the insufficiency and subjectivity of such a work. The nature of the flaws is ascribed by different experts to different causes, corresponding to local relations and individual experiences. A uniform law does not exist, but at all events the table should render service by the comparison of observations and investigations: —

[illegible]	[illegible]
[illegible] ... and [illegible]	[illegible] [illegible] In [illegible] enamel [illegible] A [illegible]
Development [illegible] scratch [illegible] formation.	[illegible] In [illegible] Defective [illegible] [illegible] [illegible] furnace. [illegible] [illegible] [illegible] [illegible] the [illegible] [illegible] [illegible] of the enamel.

POSSIBLE MISTAKES.	THEIR PROBABLE OR POSSIBLE CAUSES.
Development of hair-like cracks.	The ground enamel is too hard or too yielding in proportion to the cover-enamel. The muffle was not hot enough. The object had been burnt at the base instead of at the edges. The lime content in the clay. Too large an amount of felspar in the enamel. The enamel coated too thickly.
The object after firing has a dull lustre.	Gas emanation. The muffle walls not tight. Too large a silica, stannic oxide, or clay content. The glaze too hard. Impure acid water, when manipulating the drawing instruments. The object had been fired repeatedly, causing devitrification to set in.
B[illegible] development on the enamelled object in [illegible] more or less parallel, directions.	Flaws in the sheet metal. Crooked and [illegible] are due to defective [illegible] face of the sheet metal.
Irregular blister development.	The moist enamel has been contaminated by organic substances such as [illegible] water, etc. The crude ware was not sufficiently heated and cleaned. The clay contained organic matter. The enamel was [illegible] properly fused. The ware had been stored too long in a finished fired condition, when the glass and enamel absorbed carbon dioxide from the air and then again was fired, *e.g.* when decorated. The grinding water was contaminated. Addition of excess of vehicle to the enamel. Accessory contamination of the dried ware by organic dust, rain, etc. The metallic texture destroyed by planing or pressing.
Spot development on the fired utensil.	The utensil may have been touched before firing with a perspiring hand, whereby reduction in places of the coloured metallic oxides sets in.

This table showing the manifold possible mistakes is capable of further extension. At all events it emphasises the indispensability of absolute cleanliness, strict supervision of all the materials employed, and the thorough control of each separate stage in the process, even to the most minute detail.

CHAPTER VII.

THE DECORATION OF ENAMELLED OBJECTS—ENAMEL PAINTING.

Since the process of enamelling has no other purpose than to provide an object made from sheet or cast iron with a covering similar to porcelain in appearance, it is obvious that the enamel industry is not limited to covering utensils with one or two coloured enamels, but that attempts have also been made to utilise the secrets and art of porcelain painting. The process, from its nature, was capable of adaptation, and so it seemed desirable that the white porcelain-like enamel surface of a utensil should be decorated and painted. This new branch of enamel painting, a section of porcelain painting, has been for a long time the object of assiduous experiment and indefatigable care, with, however, continued success. He who has opportunity to admire the often artistically finished and decorated enamel wares in the show-case, will be entranced by the variety of the design and the distinguished impression which many of the decorated articles convey.

In general we may distinguish in the modern occupation of enamel painting three modes of decorating enamelled utensils: the exclusive hand-painting for especially high-class wares, decorating by means of transfers or impressions from etched steel plates (the so-called reprinting process), and finally the air-brush painting (*Spritzmalerei*).

Hand-painting in its artistic form is employed only for expensive articles such as toilet services, etc.

The preparation of ceramic transfer pictures is similar to that of chromo lithographs, using enamel colours. Chromo-lithographic impressions are transferred to paper, and since these pictures on transference would adhere badly to the enamel surface, it is provided with a thin coating of collodion, which disappears when burning in the picture.

For a long time, in porcelain and enamel painting, the technical method used for producing toned coloured surfaces was by covering the enamel colour with linseed and lavender oil, and shading away these surfaces by means of a linen pad, and this has in later years found an increased use through the discovery of air-brush painting. The coloured enamels corresponding to the best oil colours, which have been very finely ground when moist, are thrown by means of air pressure from the tube of a spray diffuser. In this way expensive coloured surfaces may be reproduced by a simple method.

By using patterns made by spray painting effective decorations are produced.

The colours used in enamel painting consist, as a rule, exclusively of an intimate mixture of natural metallic oxides (cobalt, nickel, chromium, manganese, copper, lead, tin, uranium, and cadmium oxides) or metallic salts, together with the fluxes.

The flux material, or simply flux (known as *Fondant*), is nothing more than a very easily fusible flint glass or glass of similar composition.

The fluxes frequently contain lead, since lead compounds make possible a fiery, glossy, easily fusible flux. Since the colours for decorating purposes are only used for external ornamentation, any danger due to the use of lead flux is excluded. Nevertheless, a lead-free flux is very largely employed at the present time.

The flux must have a composition suitable for the various coloured bodies.

E.g., an easily fusible flux :—

Flint	10 parts.
Red lead	8 ,,
Fused borax	40 ,,

For blue and iron red colours :—

Red lead . . .	75–80 parts.
Silica . . .	20–25 ,,

Carmine flux for carmine and purple :—

Red lead	12 parts.
Silica	33 ,,
Fused borax	55 ,,

For chromium green, blue-green, etc. :—

Red lead	73 parts.
Silica	18 ,,
Boric acid	9 ,,

Examples of an ordinary lead free flux :—

Flint	3·0 parts.
Saltpetre	2·5 ,,
Stannic oxide	4·0 ,,

Or

Silica (pure white)	6–7 parts.
Chalk	2–3 ,,
Borax	9–10 ,,

The flux is first of all melted in a crucible, finely powdered, and ground in the dry mill together with the colour substances.

The addition of coloured bodies to the flux is made in varying proportions. The majority of the enamel works obtain the enamel colours ready for use from special firms, a method more worthy of recommendation than the preparation of these bodies in the works itself.

The firing of the decorated utensil requires much care and experience, and the decoration of the ware should take place as quickly as possible, for if it be stored too long, then on firing a blister development may possibly take place.

Regarding further artistic operations there remains little more to be said, since these are too many and various, and, moreover, are dependent on the taste and experience of each separate worker.

CHAPTER VIII.

DECORATION OF THE ENAMELLED WARE—PHOTO-CERAMICS.

The intimate relation which exists between porcelain and enamel painting, as exhibited in the production of artistic effects by almost identical means and methods, suggests the similar production of photographs capable of being burnt in on enamelled objects. This kind of ornamentation has come to be a special branch of our industry, and deserves our closest attention.

The preparation of photographic coloured pictures capable of being branded meets with little difficulty.

Usually three processes are distinguished, but in practice the first is almost entirely used :—

I. Process using chromium salts :
  (*a*) The dust process (*Einstäubeverfahren*),
  (*b*) The pigment process,
  (*c*) The light printing process ;
II. Process using iron chloride ;
III. The substitution process.

The dust process, which is the most important and generally used, will now be described.

This process was invented in 1859 by two Frenchmen, Salmon and Garnier, on the principle that a mixture of potassium bichromate and gum, albumen, gelatine, etc., when exposed to the influence of sunlight, becomes insoluble.

On a glass plate covered with such a mixture, those places which are protected from the action of the light can retain a colour powder (in our case, therefore, an enamel colour) when scattered over, while the illuminated spots are not so capable. In this way, from a positive photograph on glass prepared in the usual way, a positive impression may be obtained in enamel colours, capable of being burnt in.

Six operations may be distinguished :—

1. A glass plate is covered with the mixture (chrome gelatine) sensitive to light and then dried.
2. The plate is exposed to light when under the positive.
3. The image is rendered visible by fusible colour powder, *i.e.* developed.
4. It is covered with collodion, treated with alkaline water to dissolve the chromium compounds, and transferred with the collodion layer to the enamel plate.
5. The collodion is removed by solution.
6. The image is then burnt in.

The chrome gelatine is prepared according to various formulæ. A cold saturated solution of potassium dichromate (100 grm.) in water (300 grm.) is made, and allowed to cool.

Further, a second solution is prepared from :—

Water	1 l.
Grape-sugar	50 grm.
Gum arabic	50 ,,
Honey	10 ,,
Sugar	20 ,,
Glycerine . . .	4 c.c. in summer. 3 c.c. in winter.
Alcohol	10 c.c.

Both solutions are carefully filtered, allowed to stand several hours, and the clear upper portions poured off into clean bottles.

Immediately before use (but not earlier) 100 c.c. from the first bottle are mixed with 250 c.c. from the second, and the mixture kept in the dark. A larger quantity is not prepared than will be required on the same day.

A second formula for the preparation of a fluid sensitive to light is the following :—

Water	100 c.c.
Sugar	10 grm.
Gum arabic	10 ,,
Potassium dichromate . .	4–5 ,,

Garin and Aymard, the well known French photo-ceramic experts, prescribe :—

Water	100 c.c.
Gum arabic	5 grm.
Sugar	10 ,,
Saturated solution of ammonium bichromate	25 c.c.

In damp weather a little grape-sugar is added, and in very dry weather only 15 c.c. of ammonium bichromate.

For glass plates, on which the chrome gelatine is poured, only plate-glass is used, the size of which must always be smaller than the positive, in order to avoid fracture by expansion. The plate-glass must be most carefully cleaned. The solution is poured on in semi-darkness, the plate being held inclined.

For drying purposes the plate is laid upon a thick sheet-iron slab about 15 × 20 cm., which stands on two feet of 15 cm. and two of 20 cm. in height. Underneath a spirit lamp is placed, and the whole warmed carefully for one or two minutes.

The exposure under the positive takes place in the usual copying frame, the glass side of the sensitive plate being underneath. The time of exposure in the sun is ½-1 minute, 5-10 minutes in the shade, and here a photometer may be used with advantage. The light incident on the chrome-gelatinised glass plate renders these places insoluble, and therefore the fusible colour powder strewn over by means of an absolutely dry brush will not adhere to the exposed places. The shorter the time of exposure the darker will be the picture, this being the exact opposite to the silver chloride process. After 20 to 30 seconds' exposure a veil of moisture forms, a sign that the exposure should soon terminate.

The operation is best conducted in broad daylight.

By sprinkling the colour powder the image will be slowly developed. The colour is spread over the plate several times by a brush, and no loose particles of colour must remain adhering. A correctly exposed picture develops by degrees. Through insufficient exposure and humidity of the materials a smearing of the picture may take place.

The picture is then washed to dissolve away the soluble chromium salt, and, in order not to injure the picture, a coat of collodion is given to it. After the developing process the picture may be retouched.

The transference of the image to the enamel plate is performed by the aid of leather viscose (1 litre collodion and 2-3 c.c. resinous oil). The picture is carefully freed from dust, the prepared collodion poured upon it, the picture lifted by the corners, and the glass plate laid in a dish with caustic potash solution (2 per cent.) until the yellow coloration has quite disappeared. The picture is placed in pure water, which is carefully changed twice, and to the last water a few drops of nitric acid are added to prevent the development of disturbing air-bubbles. The picture is now transferred to the enamel plate, allowed to dry, and then burnt in carefully in the muffle furnace.

Should the image be transferred with the collodion side underneath, then a reversed picture will be obtained, so that when preparing the glass positive allowance must be made. (The negative is placed reversed in the copying camera.)

If the picture lies between the enamel plate and collodion, then the latter is dissolved by means of the following mixture :—

Alcohol	50 c.c.
Ether	50 ,,
Lavender oil . . .	100 ,,
Turpentine oil . .	3 ,,

For colours the ordinary easily fusible enamel colours are used.

The second process, the process of sprinkling with iron chloride, is distinguished from the former in that the layer sensible to light becomes hygroscopic on exposure, and therefore the enamel colour adheres on the exposed places.

Poitevin offers the following formula :—

Water	100 c.c.
Ferric chloride . .	10 grm.
Tartaric acid . . .	4 ,,

The exposure lasts 5–10 minutes.

Finally, the substitution process consists in the production of a positive collodion picture according to the negative to be copied, and in this, by treatment with gold, platinum, or iridium chloride solutions, the silver is replaced or substituted by another metal. Further particulars are to be found in Dr Paul

Ed. Liesegang's *Fusible Photographic Colour Pictures* (*Photographische Schmelzfarbenbilder*).

The photo-ceramic art occupies in many senses an elevated position. After some practice the production of relatively inexpensive enamel pictures capable of resisting wear and tear may easily and quickly be performed.

CHAPTER IX

STATISTICS AND GENERAL INFORMATION

The enamelling of sheet and cast wares is almost exclusively performed by hand labour, demanding application and manual dexterity of the worker. It is a fact worthy of note that nations called progressive—that is, who follow cultured occupations and have an undeniable inclination for invention and industrial activity—possess an increasingly small enamel industry. The smallness of the enamel industry in such countries may be traced to three causes: scarcity of sufficient technical skill; more expensive mode of existence in these countries, with consequent higher wages; together with the lack of the most important mineral products necessary for producing enamels. An industry which depends on skilled hand-labour is generally not compatible with too high wages. In proportion as the wages of all places rise with the times, and as the standard of life of the worker is improved, so must greater exertion be expended in order to compensate by progress in manufacture for the increased cost due to rising wages, higher price for materials, etc. If this progress should not be caused by a rise, often too sudden, in the cost of production, then it must be due to more economical working. Experiments undertaken with the object of replacing hand-labour by the cheaper and more uniform working power of a machine have, in contrast with all other occupations, more or less missed fire in the ceramic and enamel industry. Every so-called coating machine designed for covering objects with enamel has been up to the present far removed from being a really efficient substitute for hand-labour. The difficulties in constructing such machines ridicule the inventive power of the engineer, especially those concerned with wares produced in many kinds and sizes, and in particular with the complicated rolling motion requisite for correct covering.

It may, however, be premature to exclude the possibility of sooner or later constructing a really successful coating machine, since the first steps have already been taken.

Another pressing question, full of deep concern to the interests of many firms, is the management of the works.

It is necessary in many firms to work in two sections, viz. day and night. This is so obviously a nuisance, that every firm should endeavour to work exclusively by day, with the natural exception of the furnace and some other special operations. Most enamel works, the foundation of which dates back thirty to forty years, began business in a way suitable to the condition of the industry at that time, *i.e.* on a small scale. By the unprecedented growth of our industry, it has been necessary to enlarge the plant, and this with as little disturbance as possible. These extensions always lagged behind the increasing demand for enamelled goods, with the result that in the majority of works there was a permanent lack of space, necessitating two shifts working day and night in the factory. The manifold inconveniences attached to the night-shift from a productive, qualitative, as well as from a hygienic aspect are obvious, and it is just these facts which give a certain superiority to many of the more recent firms that work only by day.

Competitors of Enamelled Kitchen Utensils. — According as a definite branch of industry is understood to be in the ascendant, caused by growing need and intelligence in the use of common utensils designed for greater convenience, so will the indefatigable inventive spirit of mankind ever seek to displace an older industry by a new invention.

The unexampled success with which the enamel industry has displaced the unsuitable, ungainly, easily broken and therefore expensive earthenware from the kitchen, has in turn encouraged others to supplant the enamelled utensil with purely metallic vessels, such as nickel, aluminium, metal-plated, and other varieties. On the whole, however, this has met with little success.

A nickel vessel will always be a luxurious kitchen utensil, and the spending capacity of the majority of consumers is limited, apart from the fact that the enamelled vessel is easily cleaned, and its appearance preferable both from a hygienic and æsthetic standpoint. The slightest amount of dirt is detected with ease.

Aluminium has generally proved disappointing, and has not fulfilled the great hopes entertained for it. More recently the proper channel for the use of aluminium has been discovered, which, however, is not to be sought for in the manufacture of household utensils, but in the great utility of the aluminium alloys for certain technical processes. Sheet aluminium is prepared to-day with a purity of 98 per cent., and exhibits among other things a peculiar behaviour towards water, and particularly towards moisture. For long the phenomenon could not be explained, viz. that aluminium utensils, which had been full of pure water, were afterwards frequently found to have undergone decomposition, forming aluminium oxide or alumina; and in like manner many an inoffensive bed-warmer made of aluminium exhibited after a little while a perforated surface. These perforations are surrounded by little white incrustations of the decomposition product, viz. alumina.

Experiments have shown that aluminium utensils which have not been most carefully dried after use (a particular in housekeeping which is never the case), under the influence of the moisture left behind and of the air, probably generate a feeble galvanic current (aluminium, nickel, or iron content = 2 per cent., and carbonic acid from the air), whereby the water is electrolytically decomposed, and the oxygen so formed causes a partial oxidation of the sheet aluminium, forming a white incrustation of aluminium oxide. If added to this is the difficult process of cleaning, the small mechanical resisting capacity of sheet aluminium, together with the price, it may safely be said that no serious competition is threatened the enamel industry from this quarter.

In another direction, too, the same applies. To the degree that our industry has progressed, by virtue of which enamelled house utensils are produced at present absolutely free from poison pleasing to the eye, durable and inexpensive, no noteworthy advance of the purely ceramic industry in the direction of manufacturing kitchen utensils can be recorded.

In addition, we have to note the versatility of the use of enamelled sheet or cast vessels for technical and hygienic purposes, such as the manufacture of door-plates, trade and industrial appliances, wainscot plates, hooks, screws, tubs, bottles, baths, wash-basins, water-closets and pipes.

Some statistical data, taken from the book by Dr Hermann Wuppermann already cited, will best illustrate the progress of the industry, especially in Germany and Austria-Hungary. To give absolutely reliable statistics of a relatively modern industry, taking into account the origin of the manufacture, the original methods pursued by different firms, wages, and balance-sheets, is a difficult matter, and only capable of partial solution. Yet every stage in this industry must be regarded as progress.

As to-day we see the ramparts of many a town pulled down to afford the inhabitants more space and possibilities of expansion, so also in the enamel industry, corresponding to its progressive development, will many a cupboard, hitherto jealously locked up, be thrown open, without injury to the industry. True progress is rather to be sought in the training of a capable works personnel, in conscientious management, and in industry and the performance of duty on the part of all those employed.

In the year 1904 there existed about 71 enamel firms in Germany, which were spread chiefly over Saxony, Rhineland, Westphalia, and South Germany. The active capital in the German enamel industry is estimated at about 2½ to 3 millions sterling. The number of workers is taken in Germany as 22,000. In Austria-Hungary 12,000 workers may find employment in the enamel industry.

In addition a large number of workers are indirectly engaged in supplying the great demand for sheet-metal, paper, chemical products, etc.

The output of the separate works is different, and depends on the locality, management, and intelligence of the workers. One firm will produce more with the same number of workers than another. Equally decisive for the output of a works is the completeness of its technical equipment. The quantity of enamelled sheet ware produced per annum in Germany is estimated at 70,000 to 85,000 tons. As an average price per kilo. of enamelled ware 8½d. is accepted.

Single enamel firms show a yearly total of £400,000 to £450,000, and it is worthy of note that there is a continual tendency to enlarge existing works.

If the average value of the forged sheet metal be stated at 24s. per 100 kg., then the average sheet-metal consumption per annum for our industry in Germany may be put at 70,000 to 85,000 tons, with a value of about £850,000 to £1,000,000 sterling.

The highest price for sheet metal was paid in the year 1899, and was 32s. per 100 kg.

The dividends paid by the larger firms vary in different years, and, for example, in one firm were 10 per cent. (1898), 12 per cent. (1899), 8 per cent. (1900), 4 per cent. (1901), 4 per cent. (1902), 5 per cent. (1903), 7 per cent. (1904).

The number of workers engaged in single firms varies from 3000 to 4000.

For lighter work many women are engaged. The dangers to the worker in the enamel industry are, apart from the crude-ware manufacture, insignificant. The average working period is ten hours, but the furnace workmen are divided into three sections of eight hours.

The customs comparisons for different countries throw considerable light on the enamel industry, which exports a part of its produce.

SUMMARY OF THE TAXES LEVIED ON ENAMELLED SHEET-METAL UTENSILS BY DIFFERENT STATES.*

Germany	7/6	per 100 kg. (per 2 cwt.).	
Austria-Hungary	42/6	„ „	
Sweden	55/0	„ „	
United States of America, about	28/0	„ „	(10% of the value).
Belgium „	10/6	„ „	(15% „ „).
France	24/0	„ „	
Switzerland	17/7½	„ „	
Russia	59/0¾	„ „	
Roumania	80/0	„ „	
Italy	24/0	„ „	
Spain	22/3½	„ „	
Turkey about	5/7½	„ „	(8% of the value).
Denmark	7/6	„ „	
The Netherlands	3/6	„ „	(5% „ „).
Great Britain	...		

Taxes on sheet iron when imported into Germany, according to the recent German tariff of 25th December, 1902 (Items 786-788), sheet metal :—

786. Crude, forged, turned, dressed, varnished : In thicknesses of more than 1 mm., 30s per ton ; in thickness of 1 mm. or under, 46s. per ton.

A comment on items 786 and 788 is important, viz. :—"For sheet iron of smaller thickness than 5 mm. which is cut otherwise than rectangular (*i.e.* rolls) the tax is increased 25 per cent."

Finally, the export of enamelled sheet utensils from Germany may be noticed.

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* The data are likewise taken from the work of Dr Hermann Wuppermann, entitled *The Industry of the Enamelled Sheet-Metal Utensils in Germany.*

ENAMELLED WARES.

		1907.	1906.	1905.	1904.	1903.	1902.
Total import .	dz.*	3,737	5,784	3,451	3,612	3,959	3,872
Value in £ sterling		18,700	26,100	13,400	13,600	14,850	18,400
From							
France . .	dz.	—	266	944	1,034	1,240	1,125
	Value		1,200	2,450	2,700	4,650	5,350
Austria-Hungary	dz.	1,820	3,406	1,531	1,571	1,613	1,434
	Value	—	16,550	7,050	7,250	6,050	6,800
Switzerland .	dz.	504	489	58	87	23	46
	Value	—	2,450	200	250	100	200
Total export : .	dz.	295,149	288,575	260,218	243,441	238,658	200,049
	Value	1,475,750	1,304,850	958,400	852,050	835,300	839,800
To							
Belgium . .	dz.	4,327	9,209	11,066	6,067	3,751	4,147
	Value	—	42,700	30,850	21,250	20,150	16,600
Denmark . .	dz.	4,147	5,201	9,207	6,744	6,349	5,439
	Value	—	23,300	33,150	23,000	22,200	21,750
France . .	dz.	4,873	5,507	5,100	5,410	6,845	5,727
	Value	—	26,650	18,400	18,950	23,950	22,000
Great Britain .	dz.	48,494	52,485	45,450	45,404	48,667	46,200
	Value	—	248,250	103,600	159,150	171,450	184,800
Italy . .	dz.	14,044	13,068	13,772	10,717	8,783	9,989
	Value	—	61,750	49,000	37,500	30,750	39,950
Holland . .	dz.	22,760	21,878	31,034	29,719	27,043	22,042
	Value		102,000	113,900	104,000	9,465	90,600
Norway . .	dz.	1,804	2,120	2,019	2,400	1,588	1,525
	Value	—	9,000	72,500	84,500	5,550	6,100
Austria-Hungary	dz.	3,447	3,823	4,697	4,151	3,759	2,560
	Value	—	17,050	16,900	14,550	131,500	10,250
Russia . .	dz.	24,101	18,005	16,326	14,123	14,430	13,437
	Value	—	85,500	58,750	49,450	50,500	53,750
Finland .	dz.	2,160	1,263	1,124	1,043	958	573
	Value	—	6,200	4,050	3,650	3,350	2,300
Switzerland .	dz.	4,550	6,212	9,604	6,650	6,202	5,452
	Value	-	29,050	34,800	23,300	21,700	21,850
Spain . .	dz.	4,511	6,390	5,062	3,754	5,614	4,723
	Value	—	30,550	18,200	13,150	19,650	18,900
Turkey in Europe	dz.	2,379	2,089	1,300	1,558	1,176	1,104
	Value	—	10,050	4,700	5,450	4,100	4,400
Turkey in Asia	dz.	1,359	2,112	1,158	1,092	935	688
	Value	—	5,450	4,150	3,800	3,300	2,750
Egypt . .	dz.	3,943	2,406	1,942	4,945	3,889	2,574
	Value	—	11,250	7,000	17,300	13,350	10,300

* Dz. stands for 2 cwt.

ENAMELLED WARES—*continued.*

		1907.	1906.	1905.	1904.	1903.	1902.
British S. Africa	dz.	4,081	4,782	4,482	4,284	11,040	9,710
	Value	—	22,050	16 150	15,000	38,650	38,800
British W. Africa	dz.	4,304	3,019	2,569	2,539	2,339	2,207
	Value	—	14,550	9,250	8,900	8,200	8,900
British India .	dz.	13,475	11,816	5,663	11,573	11,355	7,231
	Value	—	57,100	20,400	40,500	39,750	28,950
Straits Settlements	dz.	1,487	2,069	1,355	1,112	876	879
	Value	—	9,850	4,850	3,900	3,050	3,500
China .	dz.	3,477	4 797	2,136	1,109	1,982	1,457
	Value	—	23,200	7,700	4,100	6,950	5,850
Dutch Indies .	dz.	3 814	3,498	1,971	1,644	651	979
	Value	—	16,000	7,600	5,750	2,300	3,900
Argentina .	dz.	10,985	12,044	10,518	8,965	7,748	2,208
	Value		57,450	37,850	31,350	27,100	9,100
Brazil . .	dz.	16,966	13,944	11,583	10 022	7,203	7,887
	Value	—	60,800	41 700	35,100	2,540	31,550
Chili . .	dz.	10,105	7,108	7 541	5,292	5,002	3,069
	Value		33,200	27,150	18,500	17,500	12,300
Columbia .	dz.	1,899	1,989	2,108	3,018	2,008	982
	Value	—	9,400	7,600	10,550	7,250	3,950
Cuba . .	dz.	4,970	3,974	3,072	2,788	3,203	2 373
	Value	—	18,900	11,050	9,700	11,400	9,500
Mexico . .	dz.	8,261	6,957	6,520	5,487	4 546	4,426
	Value	—	33,400	23,500	19,200	15,900	17,700
Peru . .	dz.	2,905	1,989	2,218	2,226	1,411	1,667
	Value	—	6,400	8,000	7,800	4 950	6,650
Uruguay . .	dz.	2,512	1,956	1,676	774	1,310	709
	Value		9,4[illegible]	60,500	2,700	4,600	3,200
Venezuela .	dz.	1,386	1,249	1,321	2,045	1,241	688
	Value	—	5,850	4 750	7,150	4,350	2,750
U.S.A. . .	dz.	21,776	24,544	19,620	15,864	16 725	21,563
	Value	—	116 100	65,650	55 550	58,550	86,250
Federal Australia	dz.	8,799	6,808	5,332	4 507	—	—
	Value	—	32,300	19,200	10,000	—	—

The dashes in the preceding tables mean that the respective entries according to the official statistics cannot, at all events at present, be given.

We see from the foregoing tables the economic significance to which the enamel industry has attained. At the same time, however, the inference is drawn, that in proportion as our industry has spread in different countries, the natural endeavour of each government has been to protect its home industry by high import taxes. The enamel industry is therefore always compelled to capture new markets, and by strenuous labour for fresh progress, for improvements, and for more efficient methods of working, to meet the difficulties of growing competition. Yet the greater the obstacles are, even more so will the spirit of invention work for the building up of our industry, and give always to our manufacture a new direction and a new impetus. In the economic war waged in all departments of industry, the palm of victory and success will fall to those firms that study the modern technical acquisitions, and unreservedly put into practice the doctrines of technical science.

APPENDIX.

EXTRACT FROM THE HISTORY OF THE ENAMEL ARTS AND OF ENAMEL ORNAMENTATION.

FOR a complete understanding of the natural evolution of the modern enamel industry applied to iron, a knowledge of the history of our predecessors in the enamel arts and enamel painting is necessary.

The enamelling of metals is of great antiquity, and the art has probably come from the Scythians, who introduced it into China at the time of the Emperor Thäiwonti. At all events the art was known in India before its introduction into China.

The Egyptians, Phœnicians, and Assyrians had already prepared enamelled jewellery, but during the period of classical culture the art remained Oriental, since neither the Greeks nor the Romans accomplished anything noteworthy in this direction.

The principal producing countries remained the Black Sea territories of Persia and North India, and from here the Byzantines transported the art into Europe about the eleventh century. The industry flourished especially in Italy, France, and Central Germany. Already the Merovingian epoch contained the rudiments of a primitive art of enamelling bronze utensils in Byzantine fashion.

It may almost be affirmed that up to the above period the enamel arts belonged to barbaric civilisation, while at this time the Indians of the Punjaub and the Persians created truly masterpieces. These were the Sikhs of the Punjaub, who employed enamels in the artistic crafts of Central India. In Lahore, the capital of Central India, the crude enamels were prepared from most remote times, and to-day these are sent to the Indian artists in Djeipour and other places. These latter understand how to prepare truly artistic enamelled utensils, but not the crude enamels themselves. The artists of Lahore, Benares, and Lucknow still enjoy great authority.

In perfection these enamels were only equalled by the French, and but partially excelled, as we shall learn from the following short history of the enamel arts and enamel painting.

The original procedure for the preparation of artistic enamelled utensils was the so-called "champlevage." Portions of metallic objects were excavated, the intermediate parts thereby weakened were shaped into ornaments, and the cavities filled with different coloured enamels, which were then fired. After cooling, the object was ground so that the metallic edges appeared as the outline of the ornament. The "émail champlevé" was principally used in Rhineland and Limoges.

The second mode frequently employed, which at present has almost been lost, is characterised by the enamels being in cells each containing several colours, which were formed into geometrical figures, unless the intermediate spaces between the separate coloured enamel cells had been formed by metallic strips. The most antique objects discovered, made of enamelled bronze, were principally equestrian, etc. Next were found in 1866 artistic enamelled bottles in calabash form among the ruins of ancient Pinguentum (30 km. from Trieste), with medallions of Antonius the Pious (138–161).

At the beginning of the fifth century the barbarians overrunning Europe introduced another artistic enamelling method, viz. the "émail cloisonné." The ornamentation on the metallic surfaces was made with metal strips, which were soldered or gummed on, and the spaces filled with enamel, thus obtaining a brilliant mosaic. As the most antique example of this art may be mentioned the sword and jewels of Childeric, king of the Franks (465–481), discovered at Tournai in 1653.

The "émail cloisonné" was in the possession of certain families during the Middle Ages, and was then known as "electron." Justin I. (518–527) sent to Pope Hormisdas an enamelled lamp (*gabatam elektrinam*).

We have to thank the monk Theophilus,* who lived in the eleventh century, for many valuable historical communications respecting the art of enamelling. In his work Theophilus is also designated Rutgerus, whereby the theory of certain archæologists appears confirmed, viz. that a portable altar, worked in silver, which is to be found among the cathedral treasures at Paderborn, had been finished by a monk Rutcherus at Helmarshausen in Franconia about the eleventh century, who may be the Theophilus mentioned.

To the most antique objects of the "émail cloisonné," which are, together with the majority at this period, of Byzantine origin, belongs the famous iron crown of Theodolinde, crowned queen of Lombardy (A.D. 625), now in possession of the Cathedral of Monza, near Milan.

The shrine relics of the True Cross in the Church of St George at Limburg (Nassau) are among the most famous of the enamelled gold vessels. The following also belong to the eleventh century: the eight valuable enamelled gold plates which were discovered in 1860 while tilling a field in Nyitra-Ivanka, in the Neutraer Comitat, in Hungary, of which seven are to be seen in the museum at Budapest, these probably constituting the remnant of a crown; and the figures of Constantine, Emperor of the Romans, also of the Empresses Theodora and Zöe, daughters of Constantine VIII. The crown of St Stephen in the castle at Budapest, which was presented by the Emperor Michael Ducas to King Geza I. of Hungary (A.D. 1077), belongs to the most noteworthy of the Byzantine enamelled works of art.

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* *Diversarum artium schedula.*

It may be mentioned that the Byzantine enamel artists were familiar with white, fiery-red, brown-red, deep-blue, green, and black enamels.

In Germany the Byzantine art was introduced under the reign of Otto II., son of Otto the Great. Otto II. married in 971 Theophanie, a daughter of the Roman Emperor at Byzantium and granddaughter of Constantine Porphiprogenetus. To the most antique art vessels of this period belong the three gold crucifixes in the church at Essen (already of German origin), which show insufficient technical knowledge. Henry II., the Saint, encouraged the art of enamelling and brought it to a higher perfection in Germany. About this period we meet for the first time the expression "smalture" for enamel.* According to Littré, the name "émail" or "esmail" is derived from the Old High German "smelzen," "smaltzen," or "schmelzen." The Germans were the first to enamel copper objects in place of gold, whereby the art was greatly extended. At the same time the technique of the "émail champlevé" was simplified.

The difficulty of preparing certain parts of the body in enamel caused the German artists to execute the head, legs, and hands of figures in metal, and only articles of clothing in enamel. Yet a further and later development caused an economy in metal for the whole figure, only the exterior being filled out with enamel (see the church treasures in Bamberg, Cologne, and the so-called Guelph jewels, etc.). From Cologne the new Rhenish art spread from France to Verdun, where at the beginning of the twelfth century a celebrated goldsmiths' school was founded.

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* Anastasius, *The Life of Leo IV.* (Gemmis et margaritis a. c. smaltis optimis adornatum).

This school belonged to the famous Nicolas of Verdun, who, in the College of Klosterneuburg, near Vienna, prepared the altar-cover or antependium in 1181, which was recast in the fourteenth century into an altar-top.* About the time of Nicolas of Verdun the development of a specific French enamel art took place (the so-called school of Limoges).† This school rests on the Rhenish technique (champlevage), and from now onwards runs parallel with it. As an example of this period may be named a plate showing the vision of St Francis of Assisi, in the Louvre at Paris.

The enamel arts of the goldsmiths at Limoges continued to grow in importance, the artists of this town being summoned to England and other countries. This French school soon confined itself to enamelling the *fonds* (backgrounds) of artistic vases, while it deserted the real goldsmithing, *i.e.* the artistic execution of figures in gold, and quickly converted the art into an industry.

The cloisonnage of the enamel, which on account of its technique gives to ornaments and figures a certain ungainliness and imperfection, was, after an interval of a century, first supplanted by the dainty, artistic, even if expensive, "champlevage." This revival is ascribed to the art of John of Pisa (1250–1358). From Italy the art of the "émail champlevé" made its reappearance in France, Germany, and Holland. Proof specimens are to be found in the Benedictine monastery at Maibingen, near Nordlingen, in Bavaria.

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* G Heider, *The Altar-top at Klosterneuburg*, Vienna, 1860.

† Ed. Garnier, *Histoire de la Verrerie et de l'Émaillerie*; Emile Molinier, *Dictionnaire des Émailleurs*, 1885.

As further technique, the translucent "à jour cloisonné" technique must be mentioned. The most antique works of this species are found mentioned in the inventory of the Vatican (*esmalta clara, esmaillio per quod videtur dies*). A beautiful goblet of Cosroe I., king of the Persians (A.D. 579), may be mentioned among the oldest discoveries of this art.

Finally we come to the last variety of the artistic enamels, viz. to the enamel covering on previously worked metallic objects, from which art our present iron enamel technique has finally evolved. This artistic enamel first appeared in the fourteenth century in France, Germany, and Italy. In the chapel at Alt-Oetting in Bavaria is found the so-called "Golden Rossel" (steed), a magnificent specimen of this art.

The gradual decay of the art of Limoges in the preparation of "émail champlevé" began in the fifteenth century. Forced by adverse circumstances, these artists discovered an enamelling process which would resuscitate the Limoges school and its art to a new life.*

The masters of Limoges soon understood how to impress upon the artistic trade engaged in preparing enamel pictures the stamp of true art. The most famous representatives in this movement were Nardon Pénicaud (1503) and Jean Pénicaud.

About 1525 the art of enamel painting received a further impetus through the so-called "émail en grisaille." This simple process permitted the best artistic effects to be produced, and consisted essentially in that a thick black enamel layer was fused upon enchased and cleansed copper objects, on which substratum a thin layer of white, finely powdered enamel was placed, which after drying allowed the black substratum to shine through. The desired pattern is traced on this surface and the white enamel round the contour is scratched away by means of a point, so that a kind of gray silhouette was obtained, which was once more burnt in. Afterwards the artist puts on more white enamel according to the requirements of the several parts, and so magnificent plastic figures or designs are obtained.

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* Claudius Popelin, *L'Art de l'Émail*, 1868.

Among the most famous grisaille artists are the members of the Limosin family: Léonard Limosin (A.D. 1576), Léonard II. and Francois Limosin (A.D. 1646); further, the Nouailhers, viz. Pierre Nouailher, Jacques Nouailher (A.D. 1674), Pierre II. Nouailher, again, Pierre Reymond (A.D. 1584), Pierre Courteys, Noel and Nicolas Laudin (A.D. 1682).

A kind of enamel painting consists in covering a copper plate with white enamel, and decorating it before branding with pulverised metallic oxides. After firing, pictures are produced similar to those obtained in faience, using a hotter fire. Painting on enamel decreased towards the end of the seventeenth century, but acquired new life under Louis XV. The principal artists of this period are Aubert, Liot, Taunay, J. B. Weyler, the Englishman Sikes (1752), Chodowiecky, the famous Graveur (A.D. 1801, in Berlin), Zincke of Dresden, Jeremias Meyer, from Tubingen (A.D. 1789), and Collins from London.

Enamel painting in other countries affords no special items of interest up to the eighteenth century.

In Italy the art flourished in Florence, and is characterised by a special design of vessel. In Germany the once flourishing art decayed strongly in Cologne, although we meet in the eighteenth century the noteworthy works of the Augsburg and Nuremberg enamellers (collection in the Museum at the Green Vault in Dresden). As representatives of this period Melchior Dinglinger (A.D. 1731) from Ulm, Wenzel Jamnitzer (1508–1586) from Nuremberg, Christof Jamnitzer (1563–1618), Hans Muelich or Mielick, and especially David Attemstetter from Augsburg, deserve mention. The enamel pictures are usually inferior to the French works. In Vienna worked Ph. H. Schindler from Dresden (1770), the Director of the Imperial Academy, who painted chiefly *Tabatièren*. There may still be mentioned Jacob Bodmer from Nottingen (A.D. 1829, at Vienna).

In Spain enamel painting and art developed under difficulties, while the English enamels attained high credit; the enamel works at Battersea, founded by the Frenchman Etienne Théodore Janssen (1753), produced prominent works of art, characterised by their elegant design and the purity of their enamels and ornamentation. The English were the first to use the reprinting process for decorating purposes,[*] in Battersea, Worcester, and Staffordshire. The art of enamelling experienced a new impetus in France about the middle of the nineteenth century, at which time Augustine (A.D. 1832) deserves mention. Thanks to the encroachment of the national manufacture at Sèvres, the half-forgotten art of Limoges has been raised from the dead. Single artists of this period, such as Meyer-Heine, Paul Avisse, and Apoil, directly rendered eminent service. Apoil was the first to execute real masterpieces of the enamelling art on an iron substratum.

Among the more recent French representatives of the art are Christofle and Falize, also Thesmar and James Tissot.

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[*] E. Molinier, *L'Emaillerie*, 1891.